



Separative recovery with lime of phosphate and fluoride from an acidic effluent containing H_3PO_4 , HF and/or H_2SiF_6

Mbarka Gouider^{a,1}, Mongi Feki^{a,*}, Sami Sayadi^{b,2}

^a Unité de Recherche Chimie Industrielle et Matériaux, Ecole Nationale d'Ingénieurs de Sfax, BPW 1173-3038 Sfax, Tunisia

^b Laboratoire des Bio-procédés, Centre de Biotechnologie de Sfax, BPO 1177-3038 Sfax, Tunisia

ARTICLE INFO

Article history:

Received 11 October 2008

Received in revised form 6 May 2009

Accepted 14 May 2009

Available online 21 May 2009

Keywords:

Lime

Fluoride

Phosphate

Separative recovery

ABSTRACT

Fluoride content and flow-rate of fertilizer plant wastewater from phosphoric acid and/or triple super-phosphate (TSP) production lead to the discharge of several thousand tons of fluoride (F^-) per year and even more for phosphate (PO_4^{3-}). Since sustainability is an important environmental concern, the removal methods should allow phosphorus and fluoride to be recycled as a sustainable products for use as raw materials either in agricultural or industrial applications. In the present work, separative recovery with lime of these two target species was investigated. A preliminary speciation study, carried out on the crude effluent, showed that two forms of fluoride: HF and H_2SiF_6 are present in a highly acidic medium ($\text{pH} \sim 2$). Evidence that fluoride is present under both free (HF) and combined (H_2SiF_6) forms, in the phosphate-containing effluent, was provided by comparing potentiometric titration curves of a crude wastewater sample and synthetic acid mixtures containing H_3PO_4 , HF and H_2SiF_6 . In a second step synthetic effluent containing mixtures of the following acids: HF, H_2SiF_6 and H_3PO_4 , were treated with lime. The behaviour of these compounds under lime treatment was analysed. The data showed that fluoride has a beneficial effect on phosphate removal. Moreover, by acting on the precipitation pH, a "selective" recovery of fluoride and phosphate ions was possible either from phosphoric acid/hydrofluoric acid or phosphoric acid/hexafluorosilicic acid mixtures. Indeed, the first stage of the separative recovery, led to a fluoride removal efficiency of 97–98% from phosphoric acid/hydrofluoric acid mixture. It was of 93–95% from phosphoric acid/hexafluorosilicic acid mixture. During the second stage, the phosphate precipitation reached 99.8% from both acidic mixtures whereas it did not exceed 82% from a solution containing H_3PO_4 alone. The XRD and IR analyses showed that during lime treatment, a H_2SiF_6 hydrolysis occurred, instead of CaSiF_6 solid formation, leading to CaF_2 precipitate. Calcium fluoride and calcium phosphate based-by-products resulting from the two-step treatment process can be used as raw materials in several industrial sectors, such as ceramic and phosphate fertilizer industries.

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1. Introduction

Several human activities such as industries producing fertilizer, aluminium, steel, bricks, and glass, release fluoride and/or phosphate ions into the environment [1,2].

Eutrophication problems caused by phosphate, especially in enclosed water bodies [3] and the detrimental physiological effects of fluoride on human health and animals have been widely described in the literature [4–7].

Phosphate fertilizer plants produce a particular kind of effluent, owing to its aggressiveness and its composition. Indeed, this

effluent is highly acidic and contains high amounts of both fluoride and phosphate [8,9] in addition to variable contents of other species, mainly sodium, calcium, chloride and sulfate. The presence of fluoride at acidic pH makes this wastewater seriously aggressive towards skin, laboratory glassware and various metallic materials.

It is important to notice that fluoride present in such a wastewater is commonly under two forms: hydrofluoric acid HF and hexafluorosilicic acid H_2SiF_6 [10–12]. Indeed, during acidulation of phosphate rock (fluorapatite containing 3–4% fluoride and 3–5% SiO_2) to produce phosphoric acid or superphosphates (single and triple), fluoride is released as hydrofluoric acid HF, which in turn reacts with silica forming volatile gas silicon tetrafluoride SiF_4 and hydrosoluble hexafluorosilicic acid H_2SiF_6 . Both HF and H_2SiF_6 are partially carried along in the wastewaters coming from the operations of gaseous waste scrubbing and phosphogypsum transportation performed during the processing of phosphate rock.

To our knowledge, fluoride under H_2SiF_6 form was usually occulted in works dealing with the treatment of synthetic effluents

* Corresponding author. Tel.: +216 97 75 33 62; fax: +216 74 675 190.

E-mail addresses: mbarkagouider@yahoo.fr (M. Gouider), mongi.feki@yahoo.fr (M. Feki), sami.sayadi@cbs.rnrt.tn (S. Sayadi).

¹ Tel.: +216 20 79 02 12; fax: +216 74 675 190.

² Tel.: +216 98 41 95 43; fax: +216 74 87 44 52.

used to mimic fertilizer plant wastewater [9]. It is important to point out that fluoride under free (HF) and combined (H_2SiF_6) forms may not behave similarly with regard to the treatment reagent.

Despite the extensive experimental work carried out for the individual removal of fluoride or phosphate ions from their corresponding media [2,7,13,14], only one study was devoted to the treatment of an effluent modelling the fertilizer plant wastewater, i.e. containing both target pollutants [9]. However, the authors [9] have considered fluoride only under the HF form, missing out the fluoride complex of silicate. They have also used more than a precipitating agent to remove phosphate and fluoride ions.

Fluoride and phosphate contents and flow-rate of fertilizer plant wastewater from phosphoric acid and/or triple superphosphate production lead to the discharge of several thousand tons of fluoride (F^-) per year and even more for phosphate [8,9]. On the other hand, fluorapatite [$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$] and fluorite (CaF_2), (natural ores commonly used for the production of industrial phosphoric and hydrofluoric acids respectively), are considered as one of the resources that will be scarce in the near future [15]. Moreover, sustainability is an important environmental concern increasingly reflected in corporate strategy, governmental policy and international agreements [16,17]. Therefore, removal methods should allow production of phosphorus and fluoride sustainable products that can be recycled for use as raw materials in either agricultural or industrial applications [8,18–20].

Chemical precipitation is a flexible approach for contaminant removal and can be applied at several stages during wastewater treatment [13,21]. It's the most adopted method to treat highly contaminated effluent. This technology has the advantage to render the recycling of the precipitated target technically and economically feasible. In most chemical treatments, phosphorus can be removed by precipitation with a metal salt, e.g., iron, aluminium and mainly calcium salts [15]. In wastewaters with high fluoride content, the most commonly adopted method is precipitation under calcium fluoride form (CaF_2) [17], using different calcium salts (CaCl_2 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and hydrated lime $\text{Ca}(\text{OH})_2$) as precipitants.

In fertilizer industry wastewater, while the use of calcium salts or lime allows the precipitation of phosphate and fluoride together, the use of iron (III) and aluminium salts leads to selective precipitation of phosphate but inhibits subsequent precipitation of fluoride by calcium salts owing to the formation of very stable $\text{F}^-/\text{Al}^{3+}$ and $\text{F}^-/\text{Fe}^{3+}$ complexes during the phosphate removal step [9,15]. Although the use of calcium salts for P and F removal is technically feasible, it is not economically adopted because of the high cost of even the low-grade salts with regard to hydrated lime similar quality [15]. Moreover, in contrast to iron, aluminium and calcium salts, lime is the most recommended product for acidic effluent treatment since it can act as both precipitating and neutralizing agent [22]. Moreover, the calcium hydroxide also avoids enrichment of the treated water with chloride and sulfate ions [22].

Taking account of all the above, the use of lime as precipitating agent for fluoride and phosphate, can be considered as the most adapted technique for wastewaters from phosphate fertilizer plants. In this connection, one should bear in mind that the physico-chemical properties of solutions from which the phosphate and fluoride can be recovered are diverse, and they require separate studies and an individual description of the process parameters [9].

The overall research undertaken in our laboratory was designed to perfect a precipitation based-process using lime as precipitating agent and allowing (i) the treatment of a wastewater from fertilizer industry containing phosphate ions and fluoride under HF and H_2SiF_6 forms; and (ii) the “selective” removal and recovery of each target pollutant (phosphate and fluoride) in order to obtain a fluoride compound free from an excessive content of phos-

phate and vice versa. The recycling of both by-products (fluoride and phosphate compounds) as raw materials in either agricultural or industrial applications can be then possible. It is to be noted that the target industrial effluent comes from a phosphoric acid and triple superphosphate plant.

The specific aims of the current research are to compare the behaviour of HF and H_2SiF_6 against precipitation with lime and to evaluate the feasibility of the “selective” recovery of fluoride and phosphate from model solutions containing phosphate and fluoride under both HF and H_2SiF_6 forms. Evidence that fluoride is partially present in fertilizer plant wastewater under H_2SiF_6 form was beforehand provided by comparing potentiometric titration curves of a crude effluent sample and synthetic acid mixtures containing H_3PO_4 , HF and H_2SiF_6 . It is noteworthy that ion-selective electrode is the commonly used method for the determination of total fluoride coming from HF and/or H_2SiF_6 form. However, this electrode does not allow neither the specification of the fluoride form (HF or H_2SiF_6 or the both forms) nor the determination of the HF and H_2SiF_6 proportions when the two forms coexist.

2. Material and methods

2.1. Chemicals and solutions

Experiments were carried out using solutions prepared by suitable dilutions of analytical grade concentrated acids (Fluka): phosphoric H_3PO_4 85% (w/w), hydrofluoric HF 40% (w/w) and hexafluorosilicic H_2SiF_6 31% (w/w). Standardized 9.53×10^{-2} M NaOH solution, used as titrant in potentiometric titrations, was prepared from high purity sodium hydroxide (Merck). Standardization was firstly realized by titration with 0.100 M HCl (Titrisol, Merck).

Hydrated lime (calcium hydroxide), procured by Merck, was used for the precipitation tests. Demineralized water was used in all the experimental runs.

Real effluent from Tunisian fertilizer industry was also used for fluoride speciation.

For all fluoride-containing solutions, only polypropylene (PP) vessels were used for sample preparation and storage.

2.2. Potentiometric titrations

Hexafluorosilicic acid H_2SiF_6 has a complex and widely unresolved speciation [23,24]. Consequently the analysis of H_2SiF_6 -containing acid mixture is usually considered as a complicated case. For instance, analysis of the ternary mixture $\text{HNO}_3 + \text{H}_2\text{SiF}_6$ and HF was already being the subject of many recent works [24–27]. In the case of phosphate industry effluent, the presence of the poly-acid H_3PO_4 next to H_2SiF_6 and HF makes the mixture even more complex from the analytical point of view.

As far as we concerned, to ensure exactly the neutralisation reactions occurring during potentiometric titrations of acid mixtures (HF, H_2SiF_6 and H_3PO_4), the exact concentration of each individual acid solution was initially determined. Potentiometric titrations were run considering the following acidic media: (1.86×10^{-2} M H_2SiF_6), (5.07×10^{-2} M $\text{H}_3\text{PO}_4 + 3.52 \times 10^{-2}$ M HF), (5.07×10^{-2} M $\text{H}_3\text{PO}_4 + 6.63 \times 10^{-3}$ M H_2SiF_6), (3.70×10^{-2} M HF + 1.86×10^{-2} M H_2SiF_6) and (4.16×10^{-2} M $\text{H}_3\text{PO}_4 + 2.96 \times 10^{-2}$ M HF + 9.31×10^{-3} M H_2SiF_6). The titrant was the 9.53×10^{-2} M NaOH solution.

Titrations were performed by using a HF resistant glass electrode (Metrohm - 6.0421.100).

For potentiometric titration of fertilizer plant wastewater, the same titrant was used.

For each considered acidic medium, titration was performed in triplicate to ensure reproducibility of the obtained data.

2.3. Precipitation tests

2.3.1. Procedure

Phosphate and/or fluoride precipitation tests were conducted considering the following acidic media: 4.86×10^{-2} M H_3PO_4 (4625 mg/L PO_4^{3-}); 3.86×10^{-2} M HF (733.5 mg/L F^-); 6.1×10^{-3} M H_2SiF_6 (700.7 mg/L F^-); 5.77×10^{-2} M H_3PO_4 (5482 mg/L PO_4^{3-}) + 3.69×10^{-2} M HF (702.9 mg/L F^-); 5.77×10^{-2} M H_3PO_4 (5482 mg/L PO_4^{3-}) + 6.1×10^{-3} M H_2SiF_6 (700.7 mg/L F^-). These PO_4^{3-} and F^- (under HF or H_2SiF_6 form) chosen concentrations were close to those of the industrial effluent. A suspension of hydrated lime (5% (w/v)) was used and kept under continuous stirring. The initial pH was adjusted to 2.2, before starting the precipitation experiments, by adding either HCl or NaOH to the considered acidic media. During precipitation step, the lime suspension was gradually added under constant stirring until reaching the around desired pH. The mixture was stirred further for 12 h in order to ensure precipitation equilibrium. The final pH was then measured and the precipitate was separated from the slurry by vacuum filtration, washed three time with demineralized water and then dried at 105°C overnight. For each considered pH, the obtained filtrate was analysed for determining the residual F^- and/or PO_4^{3-} ion content.

Precipitation tests were performed in a pH range of 2.2–9, at room temperature ($25 \pm 2^\circ\text{C}$).

2.3.2. Analytical methods

The phosphate ion concentration was determined by using the vanado-molybdo-phosphoric acid spectrometry method [28]. The fluoride concentration was determined using the potentiometric standard method with an ion-selective electrode (Metrohm - 6.0502.150). TISAB (Total Ionic Strength Adjustment Buffer) solution was added to samples and standards to adjust the ionic strength and the pH (5.5) and to suppress complexation of fluoride ions by polyvalent cations, essentially Al^{3+} and Fe^{3+} [28]. The TISAB solution was obtained by dissolving 57 mL glacial acetic acid, 58 g sodium chloride and 4 g cyclohexane diamino-tetra-acetic acid (CDTA) in 1000 mL of demineralized water. The pH of the solution was adjusted to 5.3 with sodium hydroxide solution (5 M).

Both infrared spectroscopy (IR) and X-ray diffraction (XRD) were used to characterize the obtained precipitates. The IR spectra were recorded using an Impact 410 Nicolet spectrophotometer. The samples were used in pellet form containing 2 mg of precipitate and pressed with 200 mg of KBr. Powder XRD patterns were obtained using a Philips X'Pert diffractometer at a scanning rate of 2°min^{-1} and employing $\text{Co K}\alpha$ filtered radiation. The phases were determined by comparison with the registered patterns of the JCPDS reference data file.

The metallic species concentrations were determined by atomic absorption spectrometry (Polarized Zeeman spectrophotometer HITACHI Z-6100).

All quantitative analyses were run in triplicate for reproducibility of data and results in the figures and tables were the average ones.

3. Results and discussion

3.1. Speciation of fluoride in fertilizer plant wastewater: potentiometric titrations

The composition of the industrial effluent used in this work is given in Table 1.

Fig. 1 displays the potentiometric titration curve of this effluent (15 mL) with 9.53×10^{-2} M NaOH. As seen, three separated equivalence points appear. In order to approach the behaviour

Table 1

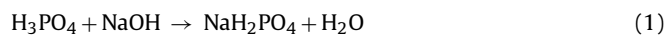
Composition (mg/L) of fertilizer plant wastewater.

pH	2
P (as PO_4^{3-})	4528
F (Total)	1225
F (as SiF_6^{2-} form)	1177
F (as "free" form)	48
Ca^{2+}	70
Mg^{2+}	68
Al^{3+}	-*
Fe^{3+}	20
Na^+	2600
K^+	78
SO_4^{2-}	1410
Cl^-	2117

* Below detection limit.

of this complex acidic medium, potentiometric titrations of the above mentioned synthetic acid mixtures containing known concentrations of H_3PO_4 + HF, H_3PO_4 + H_2SiF_6 and H_3PO_4 + HF + H_2SiF_6 were undertaken using 9.53×10^{-2} M NaOH as titrant (Fig. 2). When comparing Figs. 1 and 2, one can notice that the curves of Figs. 1, 2b and 2c display similar shapes, disregarding the titrant volumes corresponding to the different equivalence points. We can thus state that the studied effluent contains fluoride under either H_2SiF_6 or HF + H_2SiF_6 forms. On the other hand, when considering the titrant volumes obtained for the different equivalent points of curves 2a–c, and the initial concentrations of the different titrated solutions, our calculation led to the following findings:

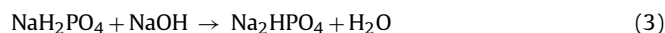
– the titration curve of HF + H_3PO_4 mixture (Fig. 2a) presents two equivalence points. The first one corresponds to both simultaneous neutralization reactions (written under simplified forms for convenience):



and



while the second is related to the following reaction:



As a rule, to separate the equivalence points of two acidities by titration, the corresponding pK_a values should differ by more than 4 units [29]. Thus, the neutralization of HF ($\text{pK}_a = 3.17$) [30] and the first acidity of H_3PO_4 ($\text{pK}_{a1} = 2.148$) yielded to a single equivalence because of the close pK_a values, while the first and the second acidities of H_3PO_4 ($\text{pK}_{a2} = 7.199$) were separately titrated [31]. It should be noted that for phosphoric acid (three-step dissociation)

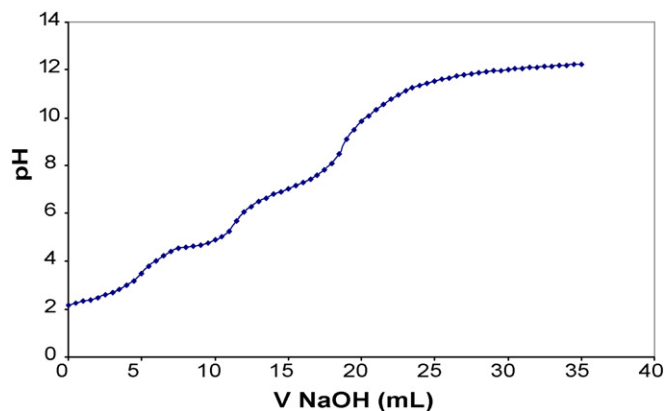


Fig. 1. Potentiometric titration curve of 15 mL wastewater with 9.53×10^{-2} M NaOH.

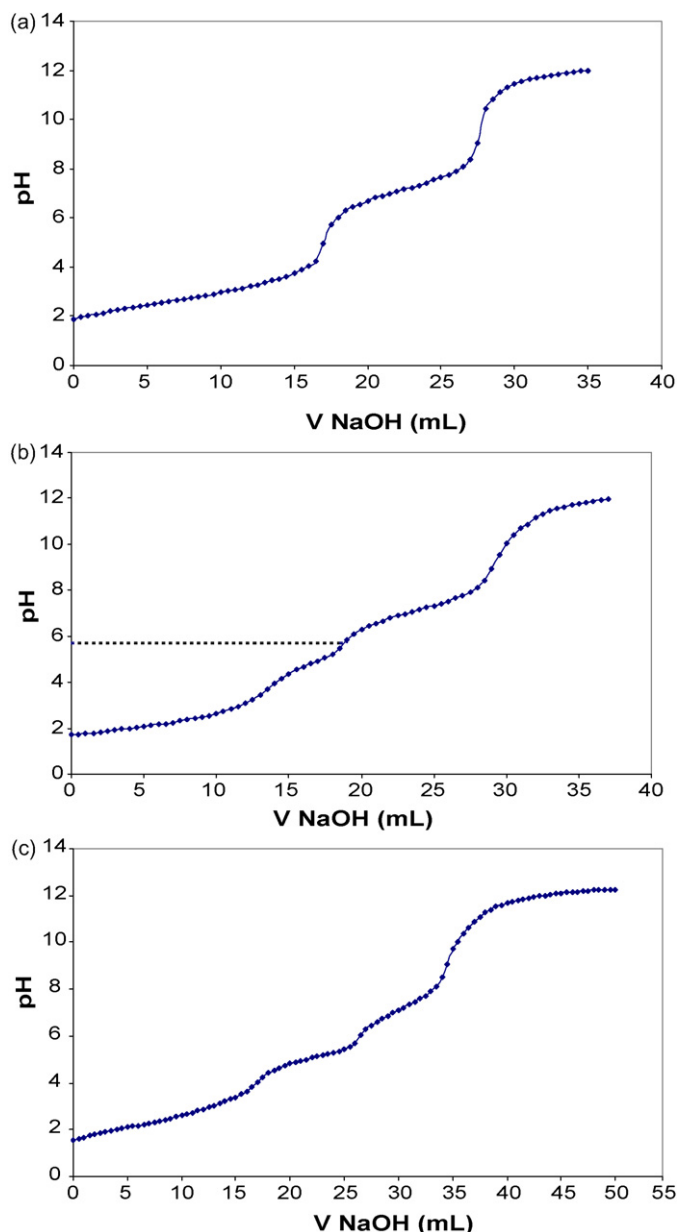
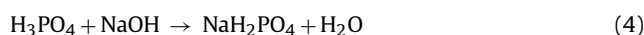


Fig. 2. (a) Potentiometric titration curve of 20 mL H_3PO_4 +HF mixture with 9.53×10^{-2} M NaOH. (b) Potentiometric titration curve of 20 mL H_3PO_4 + H_2SiF_6 mixture with 9.53×10^{-2} M NaOH. (c) Potentiometric titration curve of 20 mL H_3PO_4 +HF+ H_2SiF_6 mixture with 9.53×10^{-2} M NaOH.

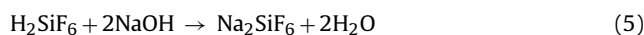
for which the third acidity is very weak ($\text{p}K_{\text{a}3} = 12.30$), only the first and the second stages were discernible in the neutralization curve. The third stage is far too weak to exhibit any point of inflexion [31].

- the three equivalence points in Fig. 2b correspond to the following reactions:

- first equivalence point:



and



- second equivalence point:

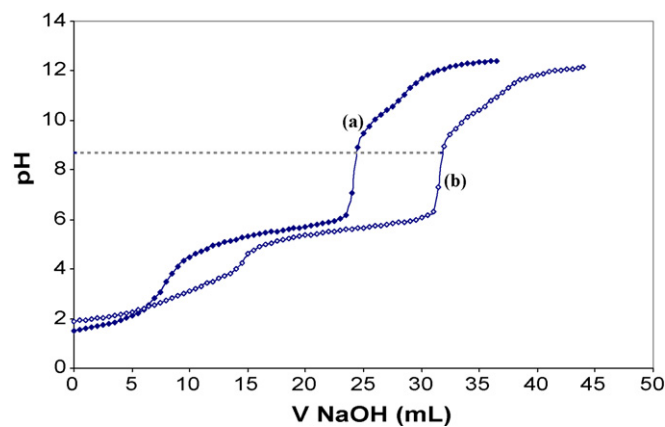
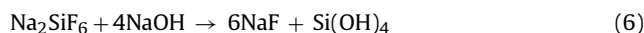
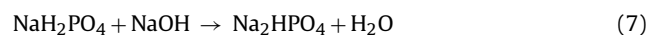


Fig. 3. Potentiometric titration curves with 9.53×10^{-2} M NaOH of 20 mL solutions containing: (a) H_2SiF_6 and (b) H_2SiF_6 +HF mixture.

- third equivalence point:

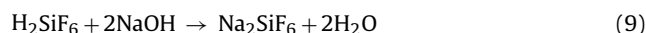


It is to be noted that H_2SiF_6 is considered as a strong acid, comparable to H_2SO_4 [23]. Its second dissociation constant $\text{p}K_{\text{a}2}$ is equal to 0.22 [23]. Thus, the first equivalence point of the titration curve (Fig. 2b) corresponding to H_2SiF_6 + H_3PO_4 mixture, includes – as in the case of H_2SO_4 + H_3PO_4 – the neutralization of both protons of H_2SiF_6 and only one from H_3PO_4 (first acidity). A further titration with NaOH yielded to the cleavage of SiF_6^{2-} ions (Eq. (6)) giving the second equivalence point in Fig. 2b. It is worthwhile to note here that the determination of the coordinates of this second equivalence point cannot be too accurate owing to the asymmetry of the corresponding titration curve.

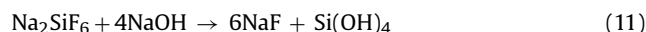
According to Fig. 2b, the hydrolysis reaction converting SiF_6^{2-} ions into silicic acid $\text{Si}(\text{OH})_4$ (equation 6), occurs at a pH-value around 5.7 (pH observed at the corresponding equivalence point), whereas it takes place at a pH around 8.6–8.7 when the titrated solution contains H_2SiF_6 alone (Fig. 3a) or in mixture with HF (Fig. 3b). A number of reports have already prominently displayed the cleavage of SiF_6^{2-} complex, in the presence of NaOH or NH_3 solutions [24,32,33] but there is still a wide spread in the mentioned pH value at which this hydrolysis reaction occurred. For example, when considering the potentiometric titration with NaOH solution of an acidic mixture containing HF+ H_2SiF_6 + HNO_3 , Henßge et al. [24] showed that SiF_6^{2-} cleavage took place in the pH range 8–9. On the other hand, other published data [32] dealing with the analysis of fluoride with ion-selective electrode in the presence of the well known TISAB solution, preconized a pH value of 8 to destroy SiF_6^{2-} complex, while others [33] stated that a pH value around 5.2–5.3 was sufficient to accomplish this hydrolysis reaction. At least part of the disagreements in the published pH values should be the nature of the considered H_2SiF_6 -containing medium (matrix effect). According to our results, the presence of H_3PO_4 in an acidic solution containing H_2SiF_6 , shifted the cleavage pH of SiF_6^{2-} species to a lower value. Independently of the origin of this pH shift, a quite meaningful consequence connected with the decrease in this pH can be evoked here. Indeed, selective precipitation of fluoride ions with lime or with calcium salts from H_2SiF_6 + H_3PO_4 mixture becomes more and more easy as the destruction of SiF_6^{2-} complex occurs at lower pHs. As far as we are concerned, experimental data related to precipitation reactions will be given later;

- for Fig. 2c, the correspondence between the equivalence points and the reactions occurring during potentiometric titration is represented below:

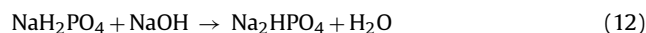
- first equivalence point:



- second equivalence point:



- third equivalence point:



Lastly, coming back to Fig. 1, the NaOH volumes corresponding to the different equivalence points showed that the crude effluent actually contains fluoride ions under both SiF_6^{2-} and F^- forms with a predominance of SiF_6^{2-} . Indeed, missing out calculation details, the obtained concentrations are:

$$[\text{F}^-] \text{ under } \text{SiF}_6^{2-} \text{ form} = 1177 \text{ mg/L;}$$

$$[\text{F}^-] \text{ under "free" form} = 48 \text{ mg/L.}$$

It should be noted that these proportions were verified using a more elaborated method based on the use of a strongly basic anion exchange resin (Amberlite IRA 400) for F^- and SiF_6^{2-} separation (Results not shown).

At this stage, it is advisable to point out that the analysis results of a yearly sampling campaign (realized during 2007's year) showed that combined and "free" fluoride contents of the wastewater fertilizer plant may fluctuate between 120 and 1260 mg/L for the former and 40–700 mg/L for the latter.

When considering the presence of sulfate ions in the industrial effluent (Table 1), one should expect that the potentiometric titration curve of this acidic medium (Fig. 1) include the neutralisation of sulfuric acid. However, such phenomenon was not taking into account for the following reason. Tunisian phosphate rock exhibits a high reactivity owing to its high carbonate content [12]. During phosphate rock decomposition in the slurry, the presence of the least little excess of free sulfuric acid leads to the phenomenon called coating: phosphate rock particles become covered by gypsum crystals, protecting them from further attack by the acids. For this reason, phosphoric acid is produced with a lack of free sulfuric acid according to the Tunisian SIAPE process [12]. Thus, the acid produced (and consequently the resulting wastewater) contains sulfate ions and not sulfuric acid. In such a medium, the SO_4^{2-} electric charges are balanced by those of metal cations such as Na^+ , Ca^{2+} , Fe^{3+} , etc.

Another consequence of the lack of free sulfuric acid is that the Tunisian acid produced (and consequently the resulting wastewater) contains a small proportion of phosphoric acid under H_2PO_4^- form. The presence of this species makes the pH of the first neutralization step (Fig. 1) related to the wastewater (pH = 3.46) slightly smaller than the pH observed (3.80) for $\text{H}_3\text{PO}_4 + \text{HF} + \text{H}_2\text{SiF}_6$ synthetic mixture (Fig. 2c).

3.2. Precipitation tests

The amount of fluoride or phosphate ions (species I) precipitated by lime was expressed in term of recovery efficiency (RE) calculated as follows:

$$\text{RE} (\%) = \frac{\text{amount of precipitated species I}}{\text{initial amount of species I}} \times 100$$

Fig. 4 depicts the pH dependence of fluoride recovery efficiency from synthetic HF and H_2SiF_6 solutions. As seen, while the RE

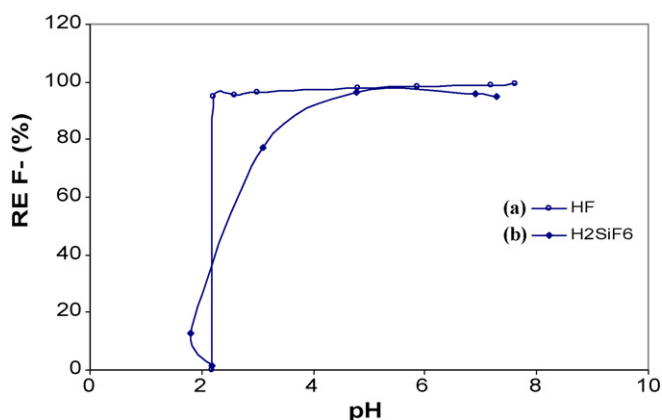
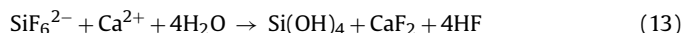


Fig. 4. Fluoride recovery efficiency from: (a) synthetic HF solution and (b) synthetic H_2SiF_6 solution.

abruptly reached a high level (94.7%) since pH = 2.2 in the case of HF solution (curve a), it gradually increased in the case of H_2SiF_6 solutions and did not attain the same level only when the pH value reached around 4.8. The effect of pH on hydrolysis extent of SiF_6^{2-} ions, is in the origin of this behaviour. Moreover, during the first stages of lime addition to the H_2SiF_6 solution, a pH decrease was observed instead of an increase (first part of curve b). This fact also owes its origin to SiF_6^{2-} hydrolysis reaction which is acidity producer. Indeed, this hydrolysis reaction can be written as:



Consequently, lime treatment of H_2SiF_6 solution leads to the precipitation of fluoride under CaF_2 form instead of CaSiF_6 . Evidence in support of this result is provided by the XRD pattern (Fig. 5) and IR spectrum (Fig. 6) of the obtained precipitate. The XRD pattern showed characteristic reflection peaks of CaF_2 (JCPDS file no.: 65-0535 for CaF_2 ; JCPDS file no.: 01-0482 for CaSiF_6). The obtained IR spectrum (Fig. 6) was also characteristic of CaF_2 [34,35]. It is to be noted that unlike CaSiF_6 which is infrared active, CaF_2 does not absorb radiations in the region between 4000 and 600 cm^{-1} [34,35]. The spectrum of CaF_2 (Fig. 6) essentially showed two bands assigned to adsorbed water: $\nu_{\text{H}_2\text{O}}$ at 3450 cm^{-1} and $\delta_{\text{H}_2\text{O}}$ at 1640 cm^{-1} . For the two small bands located between 1500 and 700 cm^{-1} , which are even present in the spectrum of analytical grade CaF_2 [34], an unambiguous assignment is difficult.

When considering precipitation pH values greater than 4.8, the RE reached more than 99% for HF solution while it did not exceed 95–96% for H_2SiF_6 one. The relatively low RE values observed in the case of H_2SiF_6 can be explained by the fact that hydrolysis reaction can be incomplete.

Fig. 7 illustrates the results obtained for PO_4^{3-} precipitation from H_3PO_4 synthetic solution and synthetic mixtures of $\text{HF} + \text{H}_3\text{PO}_4$ and $\text{H}_2\text{SiF}_6 + \text{H}_3\text{PO}_4$. As it would be seen, the presence of fluoride in the treated medium remarkably enhanced the PO_4^{3-} removal. Thus, while the RE values reached 98 and 99% from pH 4.5 for $\text{H}_2\text{SiF}_6 + \text{H}_3\text{PO}_4$ and $\text{HF} + \text{H}_3\text{PO}_4$ respectively, they did not exceed 82% for the solution containing H_3PO_4 alone even when precipitation pH reached 8 and more (Fig. 7). Moreover, a pronounced precipitation occurred at lower pHs for both mixtures when compared to the solution containing H_3PO_4 only. The enhancement of phosphate precipitation occurring in the presence of fluoride may be the result of the formation of calcium fluorophosphate solid phase(s) which is less soluble than calcium phosphate one(s) obtained for the solution containing H_3PO_4 alone. A full characterisation of the precipitated phases obtained under different pHs

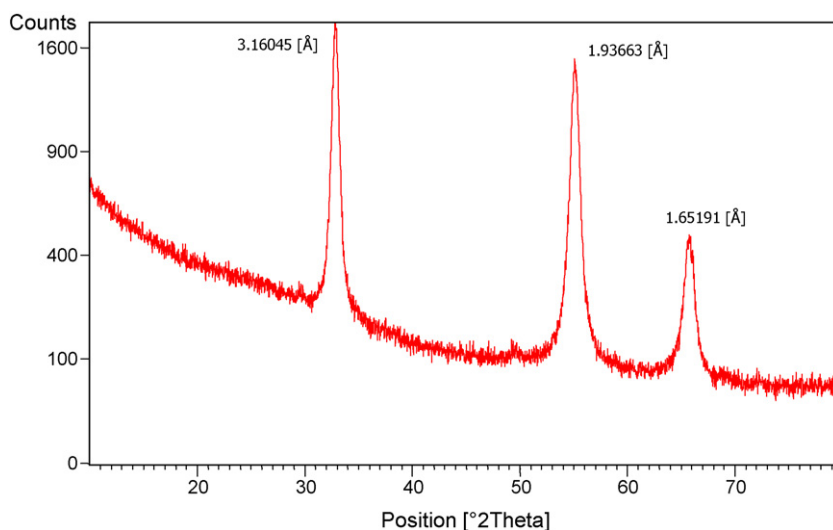


Fig. 5. XRD pattern of the precipitate (CaF_2) generated by lime treatment of H_2SiF_6 solution. Theoretical d_{hkl} (Å) for CaF_2 : 3.1581, 1.9339, 1.6492; for CaSiF_6 : 3.8300, 2.3000, 1.9100, 1.7300.

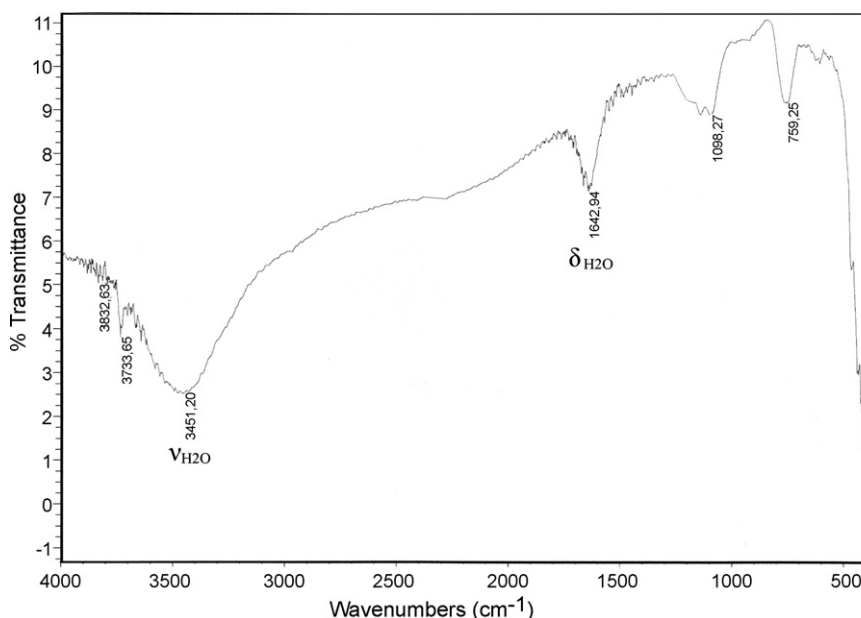


Fig. 6. IR spectrum of the precipitate (CaF_2) generated by lime treatment of H_2SiF_6 solution.

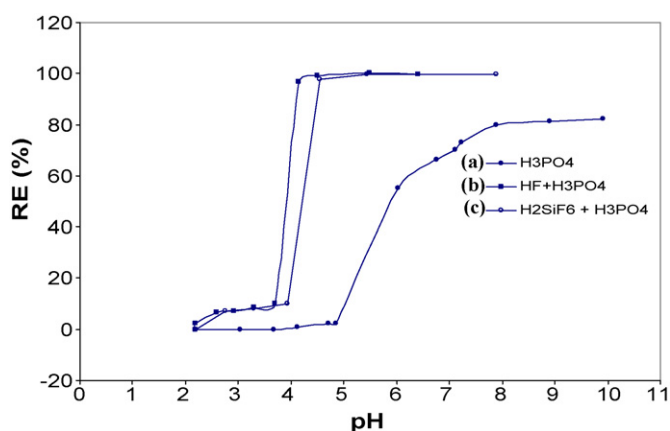


Fig. 7. PO_4^{3-} recovery from: (a) synthetic H_3PO_4 solution and synthetic mixtures of (b) $\text{HF} + \text{H}_3\text{PO}_4$ and (c) $\text{H}_2\text{SiF}_6 + \text{H}_3\text{PO}_4$.

and compositions of the treated media, using XRD, IR and ^{31}P -solid state-NMR is under investigation.

When considering the removal of both phosphate and fluoride ions from synthetic mixture of $\text{HF} + \text{H}_3\text{PO}_4$ (Fig. 8a), one can conclude that a separative precipitation of these ions is possible when acting on the precipitation pH. Hence, precipitation of calcium fluoride with small content of phosphate can be achieved in a first stage at a pH ranging from 2.6 to 3.7. In this pH interval, the RE of fluoride was of 97–98% while that of phosphate did not exceed 6–8%. In a second stage, a further addition of lime quantitatively precipitated phosphate ions only for pH values up to 4. At pH 6.4 the degree of phosphate precipitation reached 99.8% and the content of the remaining phosphate and fluoride ions in the treated solution were 8.1 and 5.3 mg/L respectively. For $\text{H}_2\text{SiF}_6 + \text{H}_3\text{PO}_4$ mixture (Fig. 8b), the separative precipitation of PO_4^{3-} and F^- contaminants is also possible but technically less easy since a high degree of separation was observed only in a narrow pH interval ranging between 3.6 and 3.9. In this pH range, the RE of fluoride and phosphate were

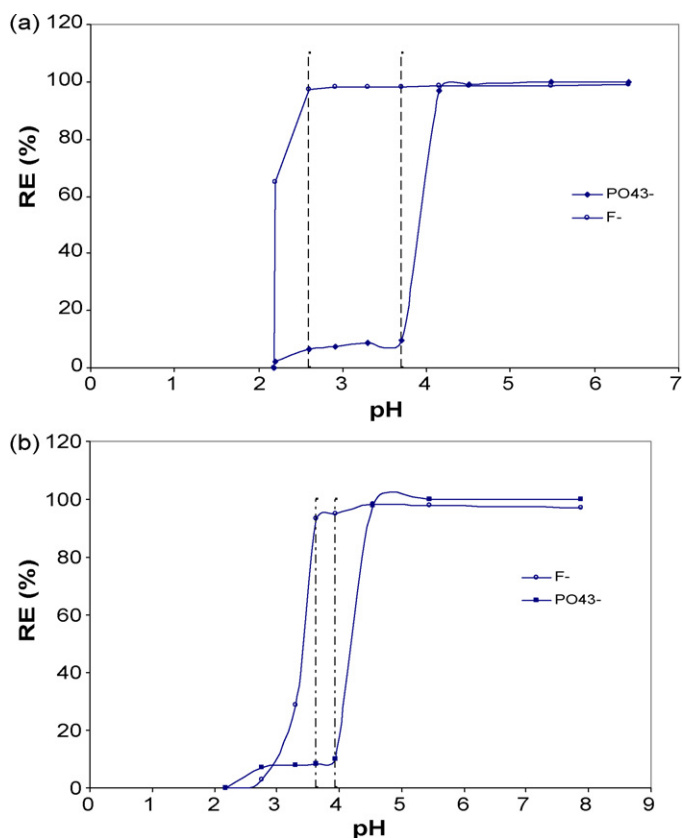


Fig. 8. (a) PO₄³⁻ and F⁻ recovery from synthetic mixture of HF + H₃PO₄. (b) PO₄³⁻ and F⁻ recovery from synthetic mixture of H₂SiF₆ + H₃PO₄.

93.2–95.1% and 8.3–9.8% respectively. At pH 5.4, the attained RE values were of 98.1% for fluoride and 99.8% for phosphate.

Regardless of the mixture considered (HF + H₃PO₄ or H₂SiF₆ + H₃PO₄), the separative precipitation of fluoride and phosphate is economically more favourable than simultaneous precipitation owing to the fact that both by-products resulting from the first process can be more easily integrated as raw materials in either agricultural or industrial applications. Indeed, technical calcium fluoride can be used as acid-grade CaF₂ (>97% CaF₂) in aluminium industry or as metallurgical-grade CaF₂ (60–72.5% CaF₂) in steel industry [8] while, calcium phosphate with fluoride content until 4% is ordinary used in phosphate fertilizer industry [12].

4. Conclusion

This work aimed to investigate the treatment by hydrated lime of model solutions imitating fertilizer plant effluent and containing H₃PO₄ and fluoride under both “free” (HF) and combined (H₂SiF₆) forms. During the addition of Ca(OH)₂ suspension to these acidic media, a cleavage of SiF₆²⁻ species occurred leading to the precipitation of CaF₂ instead of CaSiF₆. By adjusting the precipitation pH, the proposed two-step process allowed separative recovery of fluoride and phosphate ions under their insoluble calcium based-salts. The obtained two solid by-products can be used as raw materials in several industrial applications.

Acknowledgements

This work was supported by the EU project MEDINDUS Contract No: INCO-CT-2004-509159.

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