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# Optimisation of Fluorinated and Phosphorus acids stream treatment from Microelectronic industry

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The treatment of fluorinated and phosphorus acid microelectronic stream was studied by physiochemical simulations by ProSimPlus software. The conventional treatment is carry out and new systems are proposed. The precipitations of  $\text{CaF}_2$ ,  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$  (Struvite) and  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  (Hydroxyapatite) are involved. Using calcium hydroxide as carbon source and pH regulation for the precipitation of  $\text{CaF}_2$  can reduce chemical consumption more than 60%. For the Struvite precipitation, about 2,4 t/d can be recover but the effluent quality at the end is not very clean because 150 mg/L of  $\text{NH}_4\text{OH}$  is still present. Finally, the second optimization way allows to recover about 1,6 t/d of Hydroxyapatite but ammonium but be removed.

## 1. Introduction

For several years, the treatment of industrial effluents has been the subject of some studies (Bouranene et al., 2015; Friha et al., 2014). Microelectronic industries produce different types of wastewater streams which often present a very complex composition. According to Suez society, effluents of modern microelectronic industries are separated in five different streams included acids and bases stream, fluorinated and phosphorus acids stream, chemical mechanical polishing (CMP) stream and CMP copper stream which are composed of suspended solids, strong oxidants, heavy metals and organic matter, and finally the last stream contains ammonia and organic matter. Due to the very complex composition of these effluents, their treatment by the conventional activated sludge process is not feasible. So, to treat microelectronic wastewaters, different technics are employed including precipitation, chemical reactions, filtration, adsorption or ionic exchanges. It would seem interesting to optimize these treatments to increase the matter yield and to reduce energy and chemical consumption. Furthermore, especially for this type of wastewater, it would be also interesting to recover some high value-added products, which can be produced by precipitation processes, because they can be reused in several fields.

The present study is based on the simulation and optimization of microelectronic wastewaters and particularly of fluorinated and phosphorus acids stream (AFP) whose composition is reported in [Table 1](#). Models are developed for each unit operation of the treatment process, either coming directly from a commercial software (ProsimPlus) or done with user module developed for new processes that are not existing. Data taken from the literature are used to build and validate the modelling. The actual treatment of AFP wastewater is simulated as a reference and several new configurations or couplings of different types of processes will be studied.

The actual treatment of AFP stream consists in two successive precipitations to eliminate fluorine (HF), phosphorus ( $\text{H}_3\text{PO}_4$ ) and nitrogen ( $\text{NH}_4\text{OH}$ ). On a first time, the precipitation of calcium chloride ( $\text{CaF}_2$ ) is done at pH 4 with calcium chloride as carbon source and sodium hydroxide (NaOH) as pH regulation. The second

step is the precipitation of Struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) at pH 7-9 with magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) as magnesium source and NaOH as pH regulation (Ryu et al., 2008). The recovery of phosphorus from wastewater in the form of Struvite and its recycling as fertilizer in agriculture is promising. Different optimization ways are involved on this paper in order to reduce the chemical consumption, recover secondary raw materials and increase the quality of treated effluent.

## 1. Materials and methods

### 1.1 Materials

AFP stream is composed by fluorine (1000 ppm), phosphoric acid (400 ppm), ammonium hydroxide (350 ppm), sulfuric acid (1000 ppm), and acetic acid (300 ppm) (James & Gerbino, 2000). The pH of the solution is around 1-2 and the flow rate used is 100 m<sup>3</sup>/h. All simulations are done at 25°C and 1 atm.

Table 1: Composition of AFP effluent

$\text{H}_3\text{PO}_4$	HF	$\text{NH}_4\text{OH}$	$\text{CH}_3\text{COOH}$	$\text{H}_2\text{SO}_4$	pH
400 ppm	1000 ppm	350 ppm	300 ppm	1000 ppm	1-2

ProSimPlus software was used for simulations. This software allows to simulate different processes by a large choice of constituents, thermodynamic models and modules installed in the database. The main data that ProSimPlus provides to the user are the composition of flows (flow rates, concentrations) as well as the calculated thermodynamic data (temperature, pressure, enthalpy, entropy, physical state, etc...). This software has some shortcomings and it can miss some constituents or modules (membrane filtration, adsorption, or biological modules). To solve this problem, the user can create constituents in the software by himself, interact with a thermodynamic model platform and also create user modules that are fully coded with using Fortran language.

### 1.2 Methods

The actual treatment of AFP wastewater is done (Figure 1.a) and new systems are proposed (Figure 1.b and 1.c). To reduce chemical consumption, it is possible to use calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) as carbon source and pH regulation too for the precipitation of  $\text{CaF}_2$ .

Another optimisation way consists to replace the precipitation of Struvite by the precipitation of a calcium phosphate which is Hydroxyapatite ( $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ). This choice induces that only phosphate can be removed from the effluent and ammonium must be treat by another technic. Hydroxyapatite can be used in medical sector as a filler to replace an amputated bone or as a coating to promote growth within prosthetic implants.

The thermodynamic model chosen is an electrolytic model named SOUR WATER. This model can predict salts formation with data already implemented in the software. But, some minerals are absent from the database (Struvite and Hydroxyapatite) and it is necessary to add manually plenty of data for the creation of compounds and chemical reactions interacting directly with the platform. First, minerals must be created with adding for each compound, atomic data as the chemical formula and the molar mass, qualitative state at physical state at 298K, and the physical state in aqueous solution, and thermodynamic data as the solid enthalpy formation, the solid Gibbs energy formation, the solid molar volume at 298K and correlations for the solid specific heat with temperature. The data are reported in [Tables 2 and 3](#). On the other hand, it is necessary to create the formation reaction of the desired compound by ionic stoichiometric balance and add missing ions like  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$  which are necessary for the dissociation of phosphoric acid in solution and speciation reactions. For each ion, it must be mentioned the Helgeson coefficients ( $a_1$ ,  $a_2$ ,  $a_3$ ,  $a_4$ ,  $c_1$  and  $c_2$ ), the Born constant, the molar mass, the charge, and thermodynamic data as Gibbs energy formation and absolute entropy at infinity dilution. The data are reported in [Tables 4 and 5](#). Finally, correlations of equilibrium constants with temperature for the speciation and precipitation reactions must be implement. For speciation reaction, HKF (Helgeson-Kirkham-Flowers) model of the software can be directly uses.



Figure 1.a: Actual treatment of AFP stream



Figure 1.b: Introduction of  $\text{Ca}(\text{OH})_2$  as carbon source and pH regulation



Figure 1.c: Replacement of Struvite precipitation by Hydroxyapatite precipitation

## 2. Results and discussion

### 2.1 Struvite and Hydroxyapatite precipitation modules

The precipitations of Struvite and Hydroxyapatite on ProSimPlus software need some manipulations. For the creation of these two compounds, data taken from the literature of calculated must be add on the model platform. Moreover, for each compound, a solid specific heat correlation is needed. The solid specific heat correlation for Hydroxyapatite is represent by Eq(1) (Robie et al., 1979) . However, no correlation was found for Struvite, but the solid heat capacity at 298K is considered for the simulation.

Table 2: Data added for the creation of Hydroxyapatite and Struvite compounds

	Hydroxyapatite	Struvite
<b>Chemical formula</b>	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	$\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$
<b>Molar Mass (g/mol)</b>	502.32	245.4
<b>Physical state (at 298K)</b>	Solid	Solid
<b>Physical state in aqueous solution</b>	Partially Soluble	Partially Soluble
<b>Solid enthalpy formation (kJ/mol)</b>	-6,669.26 <sup>a</sup>	-3,681.9 <sup>a</sup>
<b>Solid Gibbs energy formation (kJ/mol)</b>	-6,301.5 <sup>a</sup>	-3,051.1 <sup>a</sup>
<b>Solid molar volume at 298K (cm<sup>3</sup>/mol)</b>	158.99 <sup>b</sup>	144.54 <sup>b</sup>

a. (La Iglesia, 2009)

b. database.iem.ac.ru

The solid heat capacity of Struvite is calculated by using a modified Kopp's rule Eq(2). The Kopp's rule method shows that the specific heat is the sum of the contributions for each atomic element in the compound. Hurst and Harrison determined new elemental contributions for solids (Table 3) and these values are used to calculate the solid heat capacity of Struvite (Hurst & Harrison, 1991). Misc term represent a constant associated with elements not having a specific constant.

$$C_p(\text{HAP}) = 387.76 + 0.11856 T + 1,811.2 T^{-0.5} - \frac{12703000}{T^2} \quad (1)$$

$$C_p = (\sum_{i=1}^n C_i \times N_i) + C_{Misc} \times N_{Misc} \quad (2)$$

Table 3: Elemental contributions for solids (J/mol/K)

Solids	
N	18.74
H	7.56
O	13.42
Mg	22.69
Misc	26.63

To predict a salt precipitation, data about phosphate ions are necessary (Table 4). For each ion, the Helgeson coefficient and the Born constant must be adding (Shock & Helgeson, 1988; Shock et al., 1989). Moreover, speciation and precipitation correlations within temperature for each mineral are essential. Speciation correlations can be directly given by the software using HKF model (Helgeson-Kirkham-Flowers) whereas the precipitation correlations must be determined by experiments or in this case, with data taken from the literature.

Table 4: Helgeson coefficient and Born constant for phosphate species

	$a_1^*$	$a_2^*$	$a_3^*$	$a_4^*$	$c_1^*$	$c_2^*$	$w^{**}$
$H_3PO_4$	0.82727	1,241.82	0.8691	-32,924	17.9708	17,727	-22,000
$H_2PO_4^-$	0.64875	805.95	2.5823	-31,122	14.0435	-44,605	130,030
$HPO_4^{2-}$	0.36315	108.57	5.3233	-28,239	2.7357	-149,103	333,630
$PO_4^{3-}$	-0.05259	-906.54	9.3131	-24,042	-9.475	-264,397	561,140

\* Helgeson coefficient

\*\* Born constant

Table 5: Thermodynamic data for ions

	$\Delta G^{\circ}_h$ (cal/mol)	$S^{\circ}_h$ (cal/mol/K)
$H_2PO_4^-$	-270,140	21.6
$HPO_4^{2-}$	-260,310	-8
$PO_4^{3-}$	-243,500	-53

The precipitation correlations given by Eq(3) and Eq(4) are determined with solubility data show on Figure 1.a and Figure 1.b. For each compound, from values of solubility products  $K_s$  found with temperature, it is possible to find three correlation forms proposed by ProSimPlus software but it is recommended to use the natural logarithm of  $K_s$  in function of the temperature (K) (Hanhoun, 2011; McDowell et al., 1977).

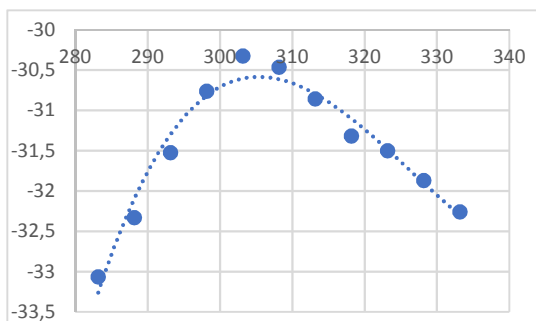


Figure 1.a : Evolution of natural logarithm of solubility product of Struvite VS temperature

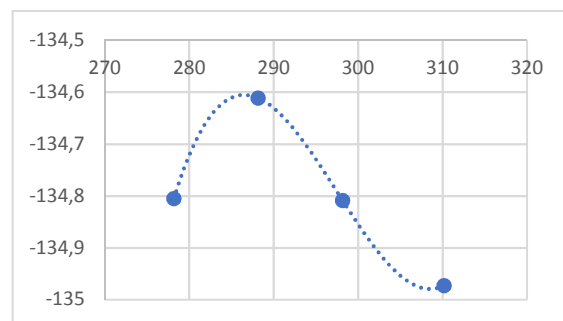


Figure 1.b : Evolution of natural logarithm of solubility product of Hydroxyapatite VS temperature

$$\ln K_s (\text{Struvite}) = 6 \times 10^{-5} T^3 - 0.0624 T^2 + 20.279 T - 2,219 \quad (3)$$

$$\ln K_s (\text{HAP}) = 7 \times 10^{-5} T^3 - 0.0623 T^2 + 18.501 T - 1,964.4 \quad (4)$$

### 3.2 Simulation results

Before simulations with ProSimPlus software, the amounts of precipitated and consumed products are determined by stoichiometric calculations to compare. Results of simulations are reported in Table 6. For the conventional treatment of AFP stream, the first precipitation permits to recover about 4,6 t/d of CaF<sub>2</sub> with use **307 kg/h** of CaCl<sub>2</sub> and **290 kg/h** of NaOH and the concentration of fluorine still present in the water is about 14,5 mg/L which is less than the limit accepted for rejection in sanitation networks (15 mg/L). The second precipitation allows to remove ammonium and phosphate compounds through the formation of Struvite. With this system, it is possible to recover about 2.4 t/d of Struvite with use 83 kg/h of MgCl<sub>2</sub>·6H<sub>2</sub>O theoretically. After the second precipitation, all phosphoric acid is consumed but it still remains about 150 mg/L of ammonium hydroxyde in the water. On the first optimisation way, calcium chloride and sodium hydroxyde are replaced by calcium hydroxyde in order to reduce chemical consumption. This configuration leads to recover the same quantity of calcium fluoride as the actual treatment but only 212 kg/h of chemical product (Ca(OH)<sub>2</sub>) is used. Results show that only **3,4 mg/L** of fluorine stay in the treated water. On the second optimisation way, precipitation of Hydroxyapatite is carry out at pH 10-11. The software indicate that it is possible to recover about 1,6 t/d of Hydroxyapatite with only 38 kg/h of calcium hydroxyde in addition to the amount already introduced for the previous precipitation, so 250 kg/h for the process.

	PSP	SC	PSP	SC	PSP	SC
	AFP		AFP 1		AFP 2	
CaCl <sub>2</sub> (kg/h)	?	185	/	/	/	/
NaOH (kg/h)	?	/	?	/	/	/
Ca(OH) <sub>2</sub> (kg/h)	/	/	212	215	250	275
MgCl <sub>2</sub> ·6H <sub>2</sub> O (kg/h)	?	83	?	83	/	/
Calcium Fluoride (t/d)	4.61	4.68	4.61	4.66	4.61	4.66
Hydroxyapatite (t/d)	/	/	/	/	1.6	1.64
Struvite (t/d)	?	2.4	?	2.4	/	/

### 3. Conclusion

The treatment of fluorinated and phosphorus acid microelectronic stream was studied by physiochemical simulations by ProSimPlus software. The precipitations of CaF<sub>2</sub>, NH<sub>4</sub>MgPO<sub>4</sub>·6H<sub>2</sub>O (Struvite) and Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH (Hydroxyapatite) was carried out. It is clear that it is so much interesting to use calcium hydroxide as calcium source and pH regulation for the precipitation of calcium fluoride. Only 212 kg/h of calcium hydroxide is used whereas **307 kg/h** of calcium chloride and **290 kg/h** of sodium hydroxide were necessary in the first configuration. Using calcium hydroxide allows to reduce more than 60% of the chemical consumption. For the Struvite precipitation, about 2,4 t/d can be recover but the effluent quality at the end is not very clean because 150 mg/L of NH<sub>4</sub>OH are still present. Finally, the second optimization way allows to recover about 1,6 t/d of Hydroxyapatite.

To optimise these treatments, it is interesting to investigate a process which is able to remove acetic acid at the end of the actual system. A biological process and specially a PBBR (packed bed biofilm reactor) was already use for this molecule and good results was obtain (Minière, 2016). In the same way, it is also possible to use a biological process to remove both ammonium and organic pollutants like acetic acid with membrane aerated biofilm reactor (MABR). Indeed, the nitrification and denitrification can transform ammonium in nitrogen gaz and heterotrophic bacteria can remove acetic acid. This configuration can be use at the end of the second optimisation way, but it can be use also at the end of the first optimisation way and of the actual treatment where ammonium is still present. These treatments are actually studied and should be coupled with treatments presented in this paper.

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