

Synthesis of fluorapatite and the effects of ferral mass on its solubility

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ABSTRACT:

Fluorapatite is a species of apatite, a mineral mainly composed of phosphate and calcium of hexagonal form, which is characterized by the presence of fluorine whose chemical formula is $\text{Ca}_5(\text{PO}_4)_3(\text{F})$. It is a source of phosphorus, but if it contains metal oxides, it makes phosphorus less available for plants. The present work aims to synthesize fluorapatite and to study the effects of Fe^{3+} , Al^{3+} and total iron mass ($\text{Fe}^{3+} + \text{Al}^{3+}$) on the dissolution of synthetic fluorapatite. The results obtained from different analyses confirmed the formation of almost pure fluorapatite. In a second step, a study of the solubility of synthetic fluoroapatite with the addition of iron ions (0; 50; 150mg), aluminum ions (0; 50; 150mg), and finally their mixtures (0; 50; 150mg), was carried out in distilled water, and then in a perchloric acid solution. The results obtained show a progressive decrease of the dissolved P_2O_5 rate in both media. They also allow to confirm the effects of metal oxides on the dissolution of rock phosphate. The rates of dissolved phosphorus expressed as a percentage of P_2O_5 of fluoroapatite in distilled water are respectively (16.89%; 3.51%; 0%, in the presence of iron); (16.89%; 0%; 0%, in the presence of aluminum); (16.89%; 0.3% ; 0%, in the presence of iron and aluminum) and in the perchloric acid solution (56.79%; 41.30%; 28.37%, in the presence of iron); (56.79%; 40.54%; 31.75%, in the presence of aluminum); (56.79%; 38.91%; 27.17%, in the presence of iron and aluminum)

Key word: Synthesis, fluorapatite, effects, ferral, solubility

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I. INTRODUCTION:

Rock phosphates refer to natural mineral assemblages containing a high concentration of phosphate minerals. The term refers to both unenriched phosphate ores and concentrated products. In addition, rock phosphate is a sedimentary deposit in the form of hydroxyapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, chlorapatite $\text{Ca}_5(\text{PO}_4)_3(\text{Cl})$ and fluorapatite $\text{Ca}_5(\text{PO}_4)_3(\text{F})$. The latter is considered as the reference compound of this family because of its stability and its existence practically in a pure state [1]. The merchant phosphate of Tahoua is a sedimentary phosphate of nodular type which is constituted mostly by fluorapatite and has an average P_2O_5 content of about 30%, with high Fe_2O_3 , Al_2O_3 , SiO_2 and organic matter contents that affect the merchantability of the nodules [2]. The merchantable phosphate of Tahoua has a low solubility in water contrary to certain natural phosphates. This low solubility is due to the presence of Fe and Al in the sample. Indeed, if their ratio $(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3) / \text{P}_2\text{O}_5$ exceeds 0.10 then the water soluble P_2O_5 is very low [3]. Within the framework of the valorization of the Tahoua commercial phosphate, we studied the effect of iron and aluminum on the solubility of a synthetic fluorapatite. The synthesis was carried out by double decomposition of calcium nitrate, sodium hydrogen phosphate in the presence of sodium fluoride. The product obtained is calcined at 600°C for 1 hour. This technique is one of the best-known processes for phosphate enrichment [4]. It is based on the dissociation of the molecules by thermal treatment. It consists in decomposing CaCO_3 into CaO and CO_2 gas to improve the structure of the fluorapatite. Several authors have shown that the main modifications of the apatite structure are the expulsion of CO_2 in the structure. This transformation is accompanied by the formation of free CaO and P_2O_5 [4]. The obtained powder was characterized by X-ray diffraction and infrared spectrometry. After the synthesis of the obtained powder, an addition of ferral masses (iron oxide, aluminum oxide and the sum of two oxides) was carried out in order to determine the effect of ferral masses on the dissolution of the synthetic fluoroapatite. An investigation was carried out to study the effect of the incorporation of metal oxides in the fluorapatite structure on the dissolution of fluorapatite in perchloric acid and in distilled water. Thus, different amounts of iron and aluminum were mixed with 0.25 g of the synthetic fluorapatite to see their effects on the solubility

II. MATERIALS AND METHODS:

In order to understand the behavior of Tahoua rock phosphate, we studied the influence of Fe^{3+} and Al^{3+} ions on the solubility of phosphate. This study will allow us to determine if the addition of such or such ion can modify the solubility of phosphate. If so, it is the Fe^{3+} or Al^{3+} ion or both that modify this solubility. It should be noted that Tahoua rock phosphate contains organic matter in addition to the ions mentioned above.

Equipment used:

The devices used during this work are:

- ✓ Molecular absorption spectrophotometer brand Evolution 300 for the determination of dissolved phosphoric anhydride;
- ✓ X-ray diffraction spectrometer;
- ✓ infrared spectrum
- ✓ oven

Experimental study:

In order to understand the behavior of Tahoua rock phosphate, we studied the influence of Fe^{3+} and Al^{3+} ions on the solubility of phosphate. This study will allow us to determine if the addition of such or such ion can modify the solubility of phosphate. If yes, it is the Fe^{3+} or Al^{3+} ion or both that modify this solubility. It should be noted that Tahoua rock phosphate, in addition to the ions mentioned above, contains organic matter. The synthesis of fluorapatite was carried out by precipitation by double decomposition of calcium nitrate tetrahydrate and sodium hydrogen phosphate dihydrate in aqueous medium. The mixture containing the precipitate was adjusted to a pH of 1.85 and then left to rest for maturation.

Synthesis of fluorapatite:

In a 250 mL beaker previously rinsed with distilled water, the calcium nitrate tetrahydrate solution and the sodium hydrogen phosphate dihydrate solution are introduced, then a sodium fluoride solution is added. The mixture is slowly stirred (100 rpm) with a magnetic stirrer for 10 minutes and kept at about 60 °C for three days, then filtered. The precipitates obtained are washed with distilled water, then dried in the oven at 110°C for 24h. Then the products are calcined at 600°C for 1 hour in the oven to improve the stability of its structure (Zhu Y., et al, 2009).

Addition of Fe^{3+} ions:

Fe^{3+} ions were introduced in the form of iron sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$). In three 250 mL flasks previously rinsed with distilled water 0.25 g of the synthesized fluorapatite is introduced to each, variable masses of iron sulfate are introduced (0; 0.050; 0.150 g). Then a quantity of distilled water (how much is the quantity of water?) was poured into each flask and the mixture was kept under stirring at about 100 rpm for 20 minutes at room temperature. At the end of the stirring, each mixture was then filtered. In order to evaluate the effect of each iron mass on the fluorapatite in demineralized water, a determination of the dissolved phosphoric anhydride (P_2O_5) level was performed on each filtrate.

Addition of Al^{3+} ions:

Al^{3+} ions were introduced in the form of aluminum sulfate $\text{Al}_2(\text{SO}_4)_3$. In three 250 mL flasks previously rinsed with distilled water 0.25 g of the synthesized fluorapatite was introduced to each, variable masses of iron sulfate (0; 0.050; 0.150 g) were introduced. Then a quantity of 200mL of distilled water was poured into each flask and the mixture was kept under stirring at about 100 rpm for 20 minutes at room temperature. At the end of the stirring, each mixture was then filtered. In order to evaluate the effect of each iron mass on fluorapatite in demineralized water, a determination of the dissolved phosphoric anhydride (P_2O_5) level was performed on each filtrate.

Addition of Fe^{3+} and Al^{3+} ions:

Fe^{3+} and Al^{3+} ions were introduced as iron sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$) and aluminum sulfate $\text{Al}_2(\text{SO}_4)_3$ simultaneously. In three 250 mL flasks previously rinsed with distilled water 0.25 g of the synthesized fluorapatite is introduced, in each of them variable masses of iron sulfate (0; 0.050; 0.150 g) are introduced. Then a quantity of 200mL of distilled water was poured into each flask and the mixture was kept under stirring at about 100 rpm for 20 minutes at room temperature. At the end of the stirring, each mixture was then filtered. In order to evaluate the effect of each iron mass on the fluorapatite in demineralized water, a determination of the dissolved phosphoric anhydride (P_2O_5) level was performed on each filtrate.

Preparation of the complexing solution:

The complexation of the dissolved phosphate ions during the attack was carried out using a complexing solution. The method used for the preparation of this solution is that of Boulahbel, H [6]. Then three solutions were prepared in 250 mL flasks and mixed in order and in equal proportions.

Determination of the dissolved phosphorus content:

In a 50 mL flask, 2.5 mL of each filtrate and 10 mL of the vanadomolybdate solution were introduced and completed with deionized water to the mark. The resulting solutions are homogenized and left to stand for 10 minutes, the time required for the yellow coloration to develop. The vanadomolybdate solution is added in excess to ensure the total complexation of all the phosphate groups contained in the collected filtrates. The optical density is read using an Evolution 300 molecular spectrophotometer at wavelength $\lambda = 430 \text{ nm}$ [4; 6; 7]. Standard solutions were prepared to plot the calibration curve absorbance = f (Phosphorus concentration) to determine the phosphorus content of the collected samples and then the P_2O_5 content is deduced.

III. RESULTTS:

Synthesis of fluorapatite

The results of the synthesis of fluorapatite by precipitation are shown in Fig 1.



Fig 1: Powder photograph of synthetic fluorapatite

Characterization of the synthesized product Study by X-ray diffraction:

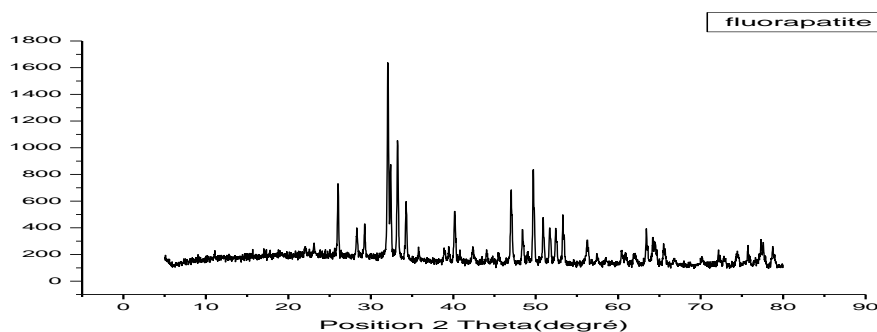


Fig 2: X-ray powder diffraction pattern of synthetic fluorapatite

Table 1: Crystallographic parameters of the obtained apatite

Apatite	Parameters	
	$a(\text{\AA}) = b(\text{\AA})$	$c(\text{\AA})$
Fluorapatite	9,363	6,878

Analysis of infrared spectra:

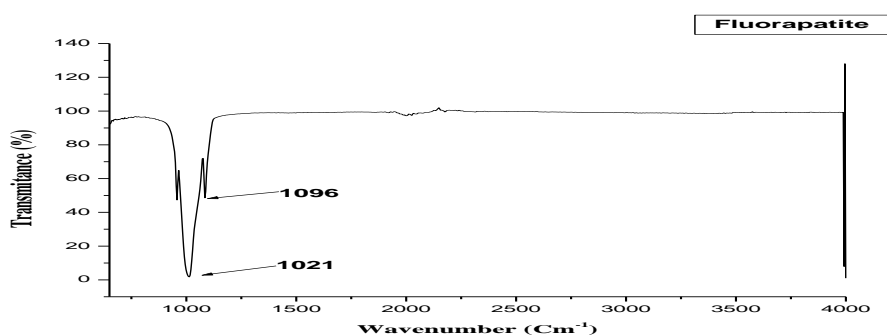


Fig 3: Infrared spectrum of synthetic fluorapatite powder

Dissolution of synthetic fluorapatite in perchloric acid and distilled water

Effect of iron on the solubility of fluoroapatites:

The effects of the addition of iron after the synthesis on the dissolution of fluorapatite are presented in fig4

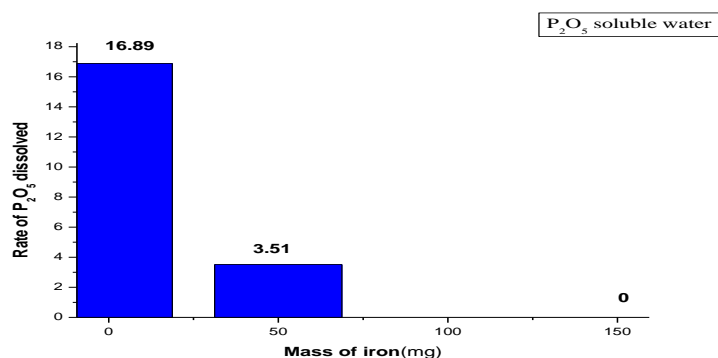


Fig 4: Rate of P₂O₅ dissolved in fluorapatite as a function of iron masses added after synthesis

Effect of aluminum on the solubility of fluoroapatite:

The dissolution of fluoroapatite in deionized water, with the addition of aluminum sulfate after its synthesis was carried out. The results obtained are presented in figure 5, which shows the rate of water soluble P₂O₅ as a function of the mass of aluminum added.

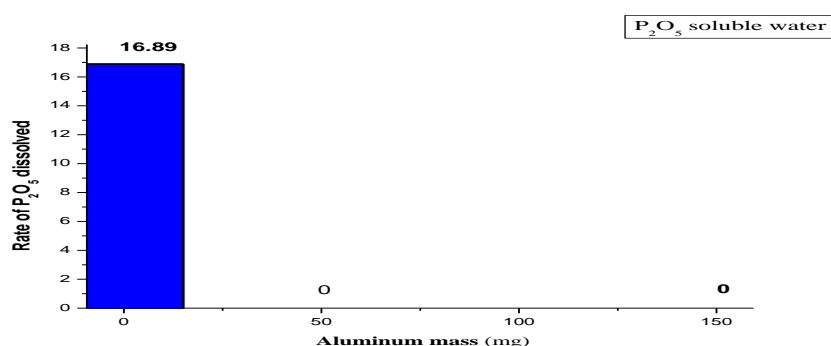


Fig 5: Rate of P₂O₅ dissolved in fluoroapatite as a function of aluminum masses added after synthesis

Simultaneous effect of iron and aluminum on the solubility of fluoroapatite

The determination of phosphoric anhydride in the filtrates resulting from the attack of fluoroapatite with the addition of a mixture of the same quantity of aluminum and iron in the synthetic fluoroapatite, by distilled water allowed to obtain the results reported in figure 6.

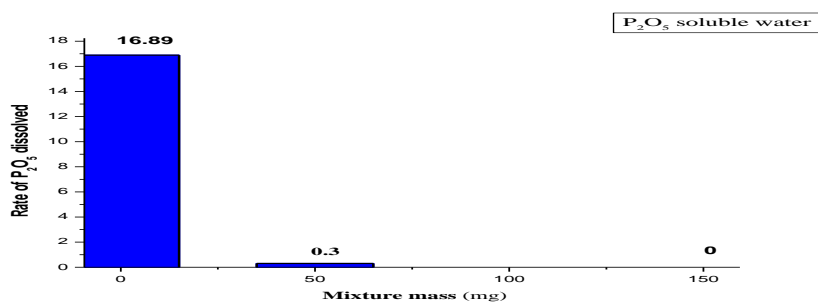


Figure 6: Dissolved P₂O₅ rate in fluoroapatite as a function of mix masses added after synthesis

Effect of iron on the solubility of fluoroapatite in perchloric acid:

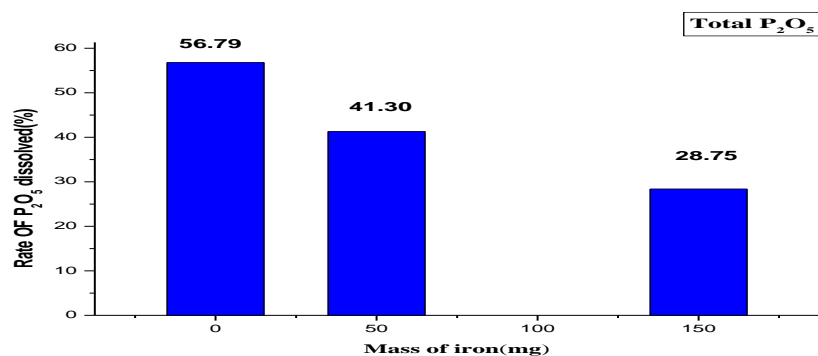


Fig 7: Rate of P₂O₅ dissolved in the fluoroapatite as a function of iron masses added after synthesis

Effect of aluminum on the solubility of fluorapatite in perchloric acid:

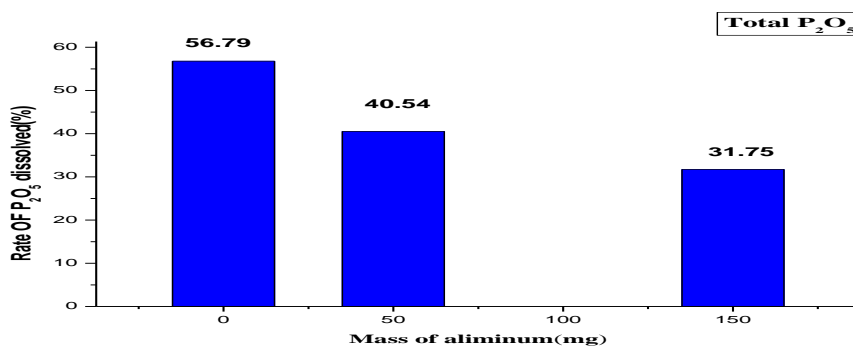


Fig 8: Rate of P₂O₅ dissolved in fluoroapatite as a function of aluminum masses added after synthesis
Action of the ferrous mass on the solubility of fluorapatites in perchloric acid

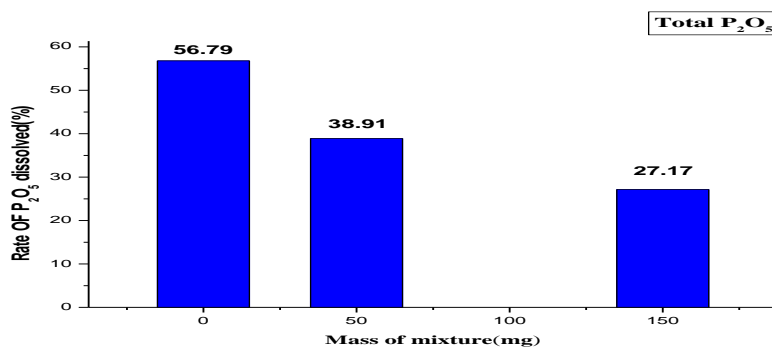


Fig 9: P₂O₅ dissolved in fluoroapatite as a function of the masses of the mix added after the synthesis

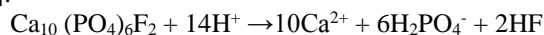
IV. DISCUSSION:

These results obtained showed a small loss in the mass of product obtained before and after calcination at 600°C for one hour. This decrease in mass could be due to the volatilization of the water of hydration and constitution of the synthesized fluorapatite [4; 8; 9; 10]. This powder obtained was used to determine the rate of total P₂O₅ and the rate of soluble P₂O₅ water with or without the addition of different amounts of metal oxides, in order to determine the effect of the ferrous mass in the fluoroapatite in particular and in natural phosphates in general.

In order to confirm the synthesis of fluorapatite, the samples were analyzed by X-ray diffraction. The X-ray diffractograms obtained (figure 2) show the existence of fluorapatite. This is confirmed by the presence of different peaks characteristic of well-crystallized apatite (23.8; 27.1; 28.5; 29.3; 32.1; 33.6; 34 .5; 36.1; 40.4; 42.6; 47.7; 49.8; 51.4; 52.5 and 53.2). These peaks are attributed to stoichiometric apatite (Ca/P = 1.65) [11]. The analysis of the results in the table below shows that the crystallographic parameters of the apatite obtained are substantially identical and close to those of a stoichiometric fluorapatite. The values of crystallographic parameters a, b and c calculated are identical to those given in the literature [11].

In order to confirm, the synthesis of fluorapatite, the samples were analyzed by Infrared. The infrared spectra of prepared products (fig 3), show characteristic bands of fluorapatite. The absorption bands located at 1021.8; 1095.8 cm⁻¹ are characteristic of PO₄³⁻ groups [4]. The absence of the broad bands located at 3570 and 3320 Cm⁻¹ which correspond to the elongation vibrations of the O-H bonds of the adsorbed water is noted. This absence is due to the fact that the analyzed product was calcined. These results confirm the structure of fluorapatite. These infrared results confirm those of the X-ray diffraction.

The decomposition reaction of fluoroapatite takes place on the surface of solid materials, it is a chemical reaction without catalyst. During the dissolution of solid materials, the bonds are broken from the weakest energetically to the least weak. Therefore, the dissolution of fluoroapatite starts with the breaking of Ca-F bonds and then Ca-P bonds. On the other hand, the P-O bonds, the most energetic, do not break so that the structure is completely destroyed [9]. In an acidic environment, the phosphate presented as PO₄³⁻ ions captures H⁺ ions to form HPO₄²⁻ or H₂PO₄⁻ ions. The decomposition reaction of fluoroapatites in acidic solutions can be written [2; 11]:



We studied the dissolution of synthetic fluorapatites with and without the addition of metal salts. The addition of some amount of ferral masses into the synthetic fluorapatite was performed to form phosphate iron, phosphate aluminum, or both simultaneously. This dissolution was evaluated through the determination of P₂O₅ in the different filtrates collected after the etching. The dissolution in perchloric acid gives us the total P₂O₅ and the dissolution in distilled water gives us the water soluble P₂O₅. The results will be represented on the figures below.

The analysis of these results shows that the rate of P₂O₅ dissolved in distilled water decreases when the amount of iron added increases, thus a decrease in the dissolution of fluorapatite. The rate of P₂O₅ soluble in water is 16.89% without addition of iron, 3.51% after addition of 50 mg of iron sulfate and 0% after addition of 100 mg of iron sulfate. This allows us to explain the low level of water soluble P₂O₅ in some natural phosphates rich in iron, in contrast to natural phosphates that do not contain enough iron. Thus, the presence of iron negatively influences the solubilization of iron-rich rock phosphates in acid solutions, especially in distilled water. Indeed, the addition of iron in the structure of fluoroapatite has clearly confirmed the effect of iron in rock phosphate. Several authors have confirmed this, especially goethite which has a high adsorption capacity that strongly influences the availability of phosphorus [5; 12; 13]. This justifies a serious problem of dissolution of Tahoua rock phosphate in water and soil. Thus, to increase the rate of water-soluble P₂O₅, iron-rich rock phosphates must undergo a specific treatment that will allow them to be soluble.

From the results obtained, we observe that the dissolution of fluorapatite synthesized with the addition of aluminum salt in water is zero while the rate of water soluble P₂O₅ of fluorapatite without the addition of aluminum is high up to 16.89%. Thus, the dissolution is practically zero if some amount of the aluminum ion is added. This shows that aluminum sulfate has a great negative effect, which prevents the solubility of fluoroapatite in particular and phosphates in general. Compared to iron sulfate, aluminum sulfate has more negative effect on the dissolution of fluorapatite. Indeed, aluminum is one of the elements that hinders the dissolution of phosphates. In addition, aluminum toxicity is a factor often invoked by several authors to explain the drop in agricultural yields especially in acidic [4; 14; 15; 16; 17 ; 19 ; 20].

These results show that the rate of water soluble P₂O₅ of pure fluorapatite (16.89%) is significantly higher than those of fluoroapatite synthesized with the addition of aluminum sulfate or iron sulfate. The rates of dissolution of fluorapatite without or with the addition of metal sulfates are 16.89%; 0.3% and 0% respectively. It is higher in fluoroapatite without mixing than those with addition in distilled water. Thus, the addition of iron and aluminum mixture in the synthesized fluorapatite causes a drop in the dissolved P₂O₅ level. Several

researchers have shown that the presence of the iron mass slows down the solubility of phosphates in demineralized water. Thus, phosphates containing a high rate of ferrous mass are confronted with a problem of dissolution. It should be noted that the ferrous mass traps the phosphate to prevent dissolution in the medium [19; 20; 21].

Dissolution of fluoroapatites by perchloric acid solutions was performed. The results obtained are presented in Figure 7. We note that the total P_2O_5 rate decreases when the iron mass increases. Indeed, the rate of total P_2O_5 passes 56.79 % for 0 mg of iron sulfate; 41.30 % for 50 mg iron sulfate; 28.37 mg iron sulfate for 150 mg oxide. This drop could be explained by the detrimental effect of the added ferric ions. Thus, this effect confirms the low dissolution of rock phosphate of several countries and especially the rock phosphate of Niger which has 8.68% of iron oxide [19], and that of Burkina Faso which has 1.75% of iron oxide [22].

Dissolution of fluorapatite by perchloric acid solutions was performed. The results obtained are presented in figure 8. We note that the total P_2O_5 rate decreases when the mass of aluminum sulfate increases. Indeed, the rate of total P_2O_5 passes 56,79 % for 0 mg of aluminum sulfate; 40,54 for 50 mg of aluminum sulfate; 31,75 mg of aluminum sulfate for 150 mg of aluminum sulfate. These results obtained are in agreement with the result obtained from the dissolution of Tahoua merchant phosphate and calcined phosphate (4.64% to 0.485 %) but contrary to iron oxide (8.68% to 14.88 %) [2]. Thus, this effect confirms the low dissolution of rock phosphate in several countries and especially Niger rock phosphate which has a content of 4.64% aluminum [19], and that of Burkina Faso which has 1.75% aluminum oxide [22], and 5.6% aluminum oxide in Togo rock phosphate [23],

Dissolution of the fluorapatites by the perchloric acid solutions was performed. The results obtained are presented in Figure 9. We note that the total P_2O_5 rate decreases when the mass of metal salts increases. Indeed, the rate of total P_2O_5 passes 56.79% for 0 mg of metallic salts; 38.91% for 50 mg of metallic salts; 27.17 mg of metallic salts for 150 mg of metallic salts. This may be due to the effect of the added ferrous mass. Thus, this effect confirms the low dissolution of rock phosphate of several countries and especially the rock phosphate of Niger which has 8.68% iron oxide and 1.84 aluminum oxide [19], and that of Burkina Faso which has 1.75% iron oxide and 3.09% aluminum oxide [22], These results obtained strengthen those found in the dissolution of Tahoua rock phosphates by sulfuric acid, citric acid and EDTA solutions [2; 5; 21; 24 ; 25].

V. CONCLUSION:

In this work, we carried out the synthesis of fluoroapatite at the temperature of 80°C by the wet precipitation method, then it was calcined at 600°C for 1 hour to improve the stability of its structure. At the end of this operation, it was noticed a decrease in the mass of synthesized products. Then we analyzed the obtained powder by X-ray diffraction and infrared spectroscopy. These results found confirm that they are the structure of fluorapatite. We also determined the dissolution of the synthesized fluoroapatite in the perchloric acid solution and in distilled water. The results obtained from the dissolved P_2O_5 levels, expressed as a percentage of phosphoric anhydride, showed that as the masses of the added metal salts increase, the dissolution of the fluorapatite gradually decreases. These results allow knowing better the effects of ions (Fe^{3+} , Al^{3+} and $Fe^{3+} + Al^{3+}$) on the solubility of synthetic fluorapatites in acid solution and especially in distilled water. These studies explain why Tahoua rock phosphate yields low levels of water-soluble P_2O_5 .

REFERENCES

- [1]. Boujier V, (2007). Influence of monohydrogenophosphate and fluorophosphate ions on phosphogypsum properties and phosphoplate reactivity. PhD thesis in Process Engineering. Ecole Nationale Supérieure des Mines de Saint-Etienne.
- [2]. Abdoul Bari I. A, (2019). Effect of thermal treatment on the solubility of Tahoua rock phosphate in sulfuric acid and citric acid. Master's thesis in mineral chemistry at Abdou Moumouni University of Niamey. 50 Pages.
- [3]. Fao, (2013). Use of natural phosphates for sustainable agriculture. Fao fertilizer and plant nutrition bulletin. Mining of rock phosphates in Khourigba, Morocco.
- [4]. Caichun Wei, Yinian Zhu, Feng Yang, Jiao Li, Zongqiang Zhu and Hongxiang Zhu, (2013). Dissolution and solubility of hydroxylapatite and fluorapatite at 25oC at different pH. Res. J. Chem. Environ. 5 Pages.
- [5]. Zhu Y., Zhang X., Chen Y., Xie Q., Lan J., Qian M. and He N., (2009). A comparative study on the dissolution and solubility of hydroxylapatite and fluorapatite at 25oC and 45oC. Chem. Geol, 268, 89-96
- [6]. Boulahbel. Hani, (2009-2010). Study of the formation reaction of simple superphosphates made from djeb phosphates. Master thesis in catalysis, Badji Mokhtar University Annaba.100 Pages.
- [7]. Mechay. A, (2014). Elaboration of nano structured apatitic biomaterials in polyol media: physicochemical characterizations and mechanical studies after compaction by spark plasma sintering. PhD thesis in chemistry from the University of Paris 13-Sorbonne Paris Cité-Institut Galilée. 152 Pages
- [8]. MANZOLA ABDOL SALAM, (1997). Precipitation of Ca^{2+} and Mg^{2+} cations by mono sodium phosphate, application to hard water treatment. Master's thesis in solid state chemistry at the University of Tunis II. 79 Pages
- [9]. Tandon, H.L.S., Cescas M.P, (1968). An acid-free vanadatemolybdate reagent for the determination of total phosphorus in soils, Soil Sci. Soc. Am. proc. in, (32), (1968), 48-51 Pages
- [10]. Claire. C., (2005). Experimental study of the kinetics and mechanisms of weathering of apatitic minerals. Application to the behavior of a minor actinide confinement ceramic. PhD thesis of the University of Toulouse III in experimental geochemistry.
- [11]. Valyasko V. M., Kogardo L. N., Khodakovskiy I. L, (1968). Stability of fluorapatite, chloroapatite and hydroxylapatite in aqueous solutions at different temperatures. Goech. Inter, 5, (1968), pp. 21-30.

- [12]. Koriko. M, (2010). Extraction, characterization, chemical reactivity of natural humic substances with Hahotoé-Kpogamé phosphates and their photodegrading properties. Physical chemistry of materials. PhD thesis from the universities of Lomé (Togo) and blaise pascal of Clermont Ferrand (France). 158 Pages
- [13]. Mustapha Hidouri a,b,* , Khaled Bouzouita a, Abdallah Aissa c, Mongi Debbabi c, (2004). Structural study of fluorapatites containing magnesium in substitution, academie des sciences published by Elsevier SAS. doi: 10.1016/j.crci.2004.04.003
- [14]. M.ARAB Hanafi, (2018). CO2 activation on hydroxyapatite. Master thesis in chemistry at the University Mouloud Mammeri of Tizi-ouzou, 39 Pages.
- [15]. El Ouardi, M., Mrani, I., Anoua, M., & Chehouani, H. (2009). Optimization of the thermal treatment of a phosphate application to the phosphate of the gantour basin in Morocco. *Materials & Techniques*, 97(2), 133-142.
- [16]. P. SEGALEN, (1964). Le fer dans les sols. Director of Research of the Office de la Recherche Scientifique et Technique Outre-Mer in Paris. 156 Pages
- [17]. PIRLOT CLÉMENCE, (2018). Effect of siderophore-induced iron oxide dissolution on phosphorus solubilization in soils. Dissertation of Master bio engineer in environmental sciences and technologies at Liege University Gembloux. 98 Pages.
- [18]. Vo Dinh Quang, Tang van Hai, E Tombo Kanyama, Je Dufey, (1996). Combined effects of aluminum, iron, and phosphorus on ion uptake and yield of rice (*Oryza sativa* L) in nutrient solution. *Agronomy*, EDP Sciences, 13 Pages
- [19]. Natatou. I, Zanguina. A, Ikhiri. K, Boos. A, Guille. J. Rastegar, F. Burgard, M; Physico-chemical characterization of Tahoua rock phosphate (Niger); *Annales de Chimie-Sciences des Matériaux*; (2005) 30: 67-76.
- [20]. Britel. O, M. Hamad, H. Chaair, S. Belouafa, K. Digua & B. Salek (2004). Synthesis of pure hydroxyapatite from phosphoric acid and calcium carbonate, Phosphorus, Sulfur, and Silicon and the Related Elements, 179:9, 1857-1865
- [21]. Issa Martin BIKIENGA Taladidia THIOMBIANO and Silas OUEDRAOGO, (2014). Feasibility study on fertilizer production in Burkina Faso from Kodjari rock phosphates. Ministry of Agriculture and Food Security.
- [22]. Natatou. I, A. Maman, A. Zanguina, I. Khalid, A. Boos and M. Burgard, (2004). Physico-chemical studies of the Tahoua (Niger) commercial phosphate. *J. Soc. Ouest-Afr. Chim*; 018; p.137-148
- [23]. Moursalou. K, Zanguina. A, Tchangbedji1. G, M. El Meray, Natatou I, Hafidi M and Sarakha. M, (2010). Study of the dissolution of phosphates from Hahotoé-Kpogamé (Togo) by natural humic acids. *J. Soc. Ouest-Afr. Chim*. 030, p. 41 - 47.
- [24]. Bassirou. I, Halidou, (2015). Comparative study of the dissolution of Tahoua rock phosphate in various mineral and organic acids. Master thesis in inorganic chemistry, Abdou Moumouni University of Niamey ,60Pages.
- [25]. Ousmane M. S, (2018). Physicochemical characterizations, improvement of agronomic efficiency by phosphocomposting of natural phosphates from Niger. PhD thesis in applied sciences, Abdou Moumouni University of Niamey.116 Pages

ABDOUL BARI IDI Awali, et. al. "Synthesis of fluorapatite and the effects of ferral mass on its solubility." *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 16(3), (2023): pp 28-35.