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Thermochemistry and Kinetics of the Reactions of Apatite Phosphates with Acid Solutions

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1. Introduction

The main component of phosphate ore derive from fluorapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, by a faint substitution of calcium by magnesium and sodium, phosphate ions by carbonate and fluorides by the latter and hydroxyl ions. Mineral component of calcified tissues (bone, dentine and enamel) derives from hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$.

Thermochemistry of these synthetic compounds and similar products began around the middle of last century (Gottshall, 1958). During the next 25 year period, few works have been performed in order to determine thermochemical quantities of these compounds, but a lot of work has been undertaken in the beginning of 70s on the synthesis and characterization of such products. Reactions of acid solutions on natural phosphates have also been widely studied, this is because these reactions lead to phosphoric acid which is the basic intermediate for phosphate fertilizer production. Fertilizers such as Mono-Ammonium Phosphate, (MAP), $\text{NH}_4(\text{H}_2\text{PO}_4)$, Di-Ammonium Phosphate (DAP), $(\text{NH}_4)_2\text{HPO}_4$, are produced by the reaction of ammonia on phosphoric acid solution. The slurry is then granulated at high temperature leading to the fertilizer product. Triple Super Phosphate (TSP) results from the reaction of phosphoric acid on the phosphate ore.

High purity (food grade) phosphoric acid is usually produced in two steps. The first one consists in reducing apatite by carbon in presence of silica at a temperature up to 1500°C , to produce native phosphorus which is then oxidized into P_4O_{10} . The latter reacts with water to produce H_3PO_4 . This process is called 'dry' process in opposition to the 'wet' one in which the phosphoric acid results from the reaction of phosphate with sulfuric acid or with a mixture of the latter with diluted phosphoric acid solution. Wet process produces an acid solution containing large amounts of impurities, some of them coming from the phosphate ore and the other from reacting acid. Depending on the reaction temperature and the concentration of the acid, the wet process produces also a by-product which can be calcium sulphate dihydrate (gypsum), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, or hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, or anhydrous Ca-sulfate, CaSO_4 , (Becker, 1989). Because of the exothermicity of the reactions occurring in this process, a large amount of thermal energy is generated allowing to heat the reaction vessel at temperature up to 120°C . Due to low cost and simplicity of acid production by wet process, fertilizers are manufactured using phosphoric acid resulting from this process.

This paper deals with the determination of the formation enthalpies of a series of apatites, the general formula of which is $\text{M}_{10}(\text{PO}_4)_6\text{Y}_2$ in which M could be Ca, Sr, Ba, Cd or Pb or a

combination of Ca with one of the other metallic elements. Y could be F, OH or Cl. A variety of products have been synthesized, characterized then dissolved in acid solution using an isoperibol calorimeter in order to determine the enthalpies of solution. Combining these quantities with others determined in the same device or picked from literature allowed to determine the enthalpies of formation. Dissolution of the two metal compounds enables to determine the enthalpies of mixing of the limit products in the solid state. Some other experiments have been recently performed on B-type Ca-carbonate apatites and allowed to characterize the substitution of PO_4 by CO_3 ions.

Dissolution of samples of fluorapatite at different temperatures has also been followed microcalorimetrically using a C 80 SETARAM microcalorimeter and kinetic models have been proposed in accordance with the thermogenesis curves. In addition attack of a phosphate ore sample by phosphoric and phosphoric/sulphuric acid solutions has been performed and revealed various phenomena which have not been previously reported.

2. Synthesis of the apatites

Two main procedures have been used in order to synthesize the products. The 'wet' one consists in adding drop by drop a solution of metal nitrate solution into a boiling diammonium phosphate solution at a pH between 9 and 11. Precipitation is then performed by maintaining ebullition for at least one hour, then the solid is separated and ignited at various temperature, depending on the product in concern. This procedure which is called as 'direct method' allows to synthesize hydroxyapatites with cadmium (Ben Cherifa, 2002) or lead (Ntahomvukiyé, 1997)- It also permitted to obtain (Ca,Cd) and (Ca,Sr) hydroxyapatite solid solutions. The reverse method consisting in dropping the metal solution into phosphate solution allows to synthesize hydroxyapatites containing only Ca or Pb, or Ca-Sr (Ben Cherifa and Jemal, 2004) or Ca-Pb (Ntahomvukiyé, 1997) couples..

Fluorapatites containing one or two metals have also been prepared according to one or the other method but the phosphate solution has been previously added with ammonium fluoride. This procedure allowed to synthesize Ca, Pb and Sr fluorapatites or Ca-Sr (Khattech and Jemal, 1997), Ca-Cd (Ben Cherifa et al, 2001a) or Ca-Pb (Ntahomvukiye et al, 1997a and 1997b) fluorapatites solid solutions.

Chlorapatites have been usually obtained by the 'solid state' procedure which consists in igniting during several hours at a temperature up to 1100°C a mixture of trimetallic phosphate $\text{M}_3(\text{PO}_4)_2$ with MCl_2 . This procedure allowed to synthesize $\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$ (Ben Cherifa 2002), $\text{Ba}_{10}(\text{PO}_4)_6\text{Cl}_2$ (Khattech, 1996), $\text{Cd}_{10}(\text{PO}_4)_6\text{Cl}_2$ (Ben Cherifa and Jemal, 2001b) together with Ca-Cd and Ca-Sr chlorapatite solid solutions.

3. Isoperibol calorimeter

The solids have been dissolved at 25°C in a 9% weight nitric acid solution using an isoperibol calorimeter which is composed of a 500mL Dewar flask immersed in a thermostated bath. In this device, the heat effect results in a variation of the temperature of the reactional medium, which is detected by a thermistance probe acting as one of the four arms of a Wheatstone bridge connected to a recorder through a '177 Keitley' current amplifier. The device is provided with an electrical resistance connected to a stabilized DC current supplier. The magnitude of the current was measured by a A.C power-meter 'GPM-8212' and the heat duration was accurately measured using a digital electronic timer with

0.01 s resolution. 350 mL solution are introduced in the flask, and the solid is preliminarily isolated in a Pyrex ball manufactured at the extremity of a 5 mm diameter tube which is supplied with a thin bar aimed at breaking the ball to start the reaction.

Experiments started by searching a quasi-steady state in which the electrical current is practically nil and the baseline deviates slightly from the horizontal line. Injection of electrical or chemical energy in the medium results in a deviation of the signal, which then becomes parallel to the previous baseline. Energy resulting from the reaction is calculated considering the corresponding shift between the baselines and the mean calibration coefficient. Calibration coefficient 'E' is calculated by dividing the calibration energy (J) over the resulting shift 'd' (mm) on the recorded paper. Three calibration experiments are usually performed and the error on enthalpy is determined considering the scatter between the extreme values of 'E'.

Various amounts 'm_i' (mg) of each product were dissolved in the same volume of solution and the molar dissolution enthalpy 'ΔH_i' was determined. Enthalpy per mass unit was calculated according to a mathematical treatment in which the statistical weight of an experimental result depends on the corresponding variance. This procedure leads to express the dissolution enthalpy as: $\Delta_{\text{sol}}H = (\sum_i w_i m_i \Delta H_i) / (\sum_i w_i m_i^2)$, in which w_i is the variance, it was here assimilated to the reverse of the square of the error. The theoretical basis of this calculation was developed by Sands, 1974 and Pattengill and Sands, 1979.

4. Thermochemistry of the apatites

4.1 Formation enthalpy of non substituted apatites

In order to determine the enthalpy of formation of any compound from dissolution results, one procedure consists in considering a particular reaction involving the compound to be studied and other solid or liquid reactants and products for which the formation enthalpies are reported in literature. This reaction can be possible, impossible or even hypothetical. Measurements of the heat evolved on dissolution of the whole constituents in the same solvent enable to derive the enthalpy of this reaction, and so, to deduce the formation enthalpy of the product in concern. This way of doing is useful particularly when dissolution enthalpy value depends on the concentration of the resulting solution that is when interaction of ions in the final solution is dependent on their concentrations even when the latter are very low. In that case the formation enthalpy of the compound have to be calculated by considering values corresponding to infinite dilution. This is the case when dissolving whitlockite, Ca₁₈Mg₂H₂(PO₄)₁₄. This compound can be involved in the following reaction:



Dissolution of various amounts of whitlockite and of stoichiometric mixture of Ca and Mg phosphates have been performed in a 46% weight HNO₃ solution using a conduction calorimeter (Calsol) and the results are reported in figure 1. Least square processing method led to express the standard molar enthalpies 'y' versus the final concentration 'x' as $y = ax^2 + bx + c$, from which the enthalpy of (R1) reaction was deduced at infinite dilution as ΔH°(298) = -203.3 ± 1.6 kJ mol⁻¹, leading to -27.93.10³ kJ mol⁻¹ as the standard enthalpy of formation of whitlockite (Ben Abdelkader et al., 2004).

Variation of dissolution enthalpy on final concentration can be neglected when the drawing of the enthalpy resulting from dissolving various amounts 'm' of the same product is linear versus 'm'. This was the case for more simple apatite compounds.

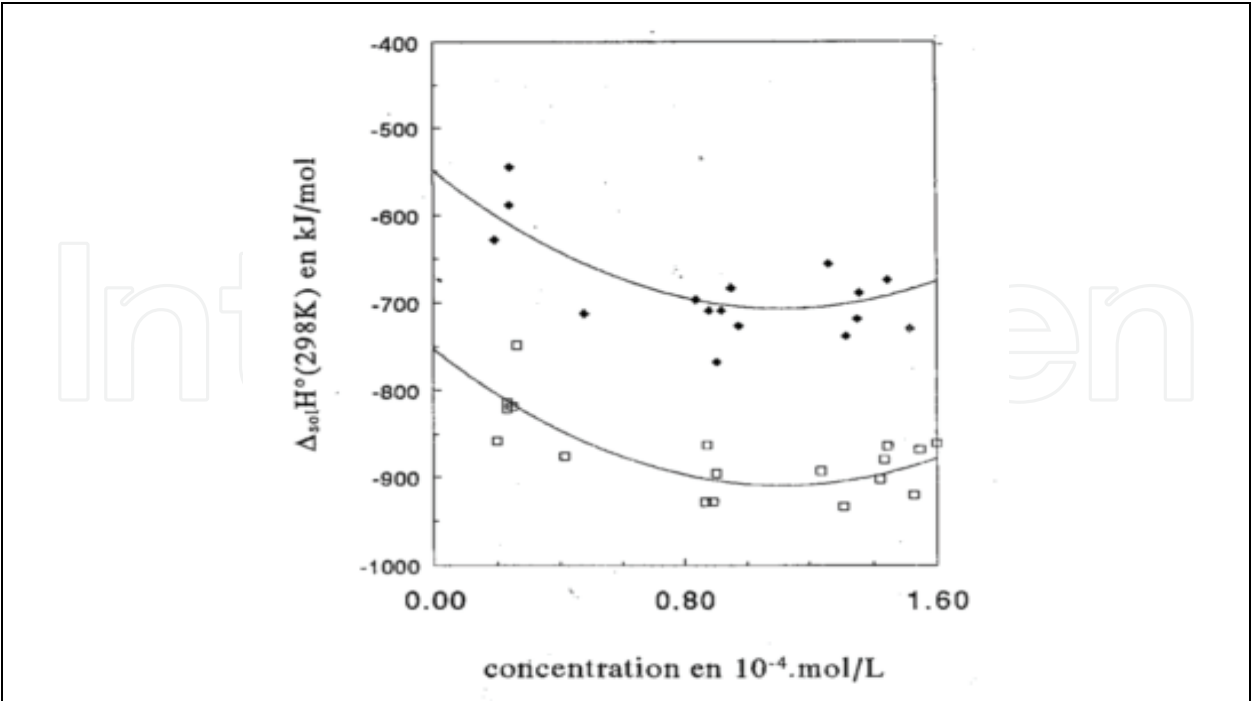
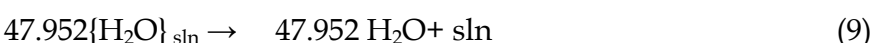
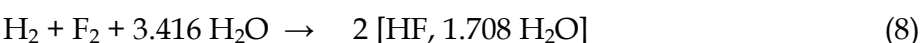
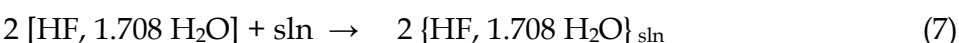
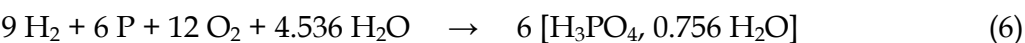
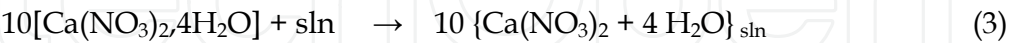
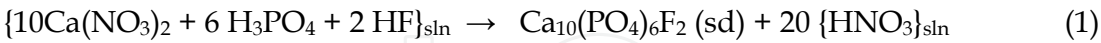
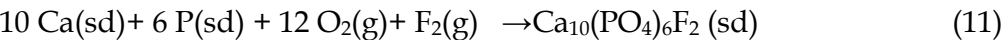


Fig. 1. Variation of molar enthalpy of dissolution of whitlockite (■) and of the stoichiometric mixture (□) as a function of the solid concentration in the final solution. Solvent : 46%weight HNO₃ aqueous solution.

Determination of the enthalpy of formation using dissolution results can also be performed by involving the entities or compounds appearing in the dissolution reaction in other processes (dissolution, dilution or mixing) in order to get a succession of reactions the “summation” of which leads to the formation reaction of the product in concern. This way of doing allowed us to determine the enthalpies of formation of a number of hydroxy, chloro, carbonate and fluor-apatites. For example, in order to determine the formation enthalpy of Ca-fluorapatite, Ca₁₀(PO₄)₆F₂, one can imagine the following succession of processes.





The subscript ‘sln’ means ‘in solution’ which is here a 9%weight HNO₃ aqueous solution, or [HNO₃, 35.35 H₂O]

In this succession, step (1) is the reverse of the fluorapatite dissolution. That dissolution is supposed to lead to a solution containing dissolved calcium nitrate, phosphoric and fluorhydric acids. Steps (2), (4), (6), (8) and (10) correspond to the formation of particular products or entities, the corresponding enthalpies are picked from literature (Handbook of Chemistry and Physics, 2006/2007). Steps (3), (5) (7) and (9) correspond to dissolution of Ca-nitrate tetrahydrate in the same solvent and dilution of H₃PO₄ and HF solutions and water in the same solvent, respectively. The corresponding enthalpies are measured in the same device using the same procedure as for the apatite. Step (11) corresponds to formation reaction of Ca₁₀(PO₄)₆F₂ according to the definition. Enthalpy of formation of chlorapatite has been determined with a similar succession but HF solution in step (7) has been replaced by a HCl solution.

This way of doing enabled to determine enthalpies of formation of various apatites and the results are gathered in table 1. However, due to lack of uncertainties on literature values, errors on these quantities can not be estimated.

M ₁₀ (PO ₄) ₆ Y ₂	Y = F	Y = OH	Y = Cl
Ca ₁₀ (PO ₄) ₆ Y ₂	-13548	-13305	-13179
Sr ₁₀ (PO ₄) ₆ Y ₂	-13604	-13373	-13233
Ba ₁₀ (PO ₄) ₆ Y ₂	-13564	-13309	-13246
Cd ₁₀ (PO ₄) ₆ Y ₂	-8795	-8648	-8463
Pb ₁₀ (PO ₄) ₆ Y ₂	-8529	-8261	-8204

Table 1. Standard enthalpies of formation (in kJ mol⁻¹) of the apatites at 25°C

More recent determination of the formation enthalpies for Ca-hydroxy and chlor-apatites led to -13399 kJ mol⁻¹ and -13231 kJ mol⁻¹ (Cruz et al., 2005). These values differ from that of table 1 by 0.7% and 0.3% respectively.

Neglecting the entropy factor, one can notice the following remarks:

- i. whatever is the metal, fluor compound is more stable than hydroxy one which is more stable than the chlor- compound. This gives an explanation of what was observed experimentally, that is, as soon as fluor is introduced in the precipitation medium, fluor compound precipitates. On the other hand, except for lead, chlorapatites were prepared only by solid state reactions because in the ‘wet’ procedure hydroxyapatites precipitate even in presence of choride ions.
- ii. for the same ‘Y’, alkali earth compounds are more stable than cadmium one which is more stable than the lead one.

Values in this table have been used by Flora et al. (2004) to determine the lattice enthalpies of these compounds and to derive consistent values for the enthalpy of formation of (PO₄³⁻, g) using the cycles reported in figure 2.

Using the correlation of Jenkins and Glasser (2003), Flora et al. calculated standard Gibbs energy of dissolution of a series of apatites including those which are not yet synthesized. A negative value of this quantity indicates a significant solubility for the apatite. This is the

case for zinc and magnesium apatites, leading the authors to conclude on 'the uncertain existence of these apatites'. In fact a significant solubility of an apatite suggests impossibility of synthesizing it by 'wet' procedure, but this does not eliminate the possibility of synthesis by solid state reaction.

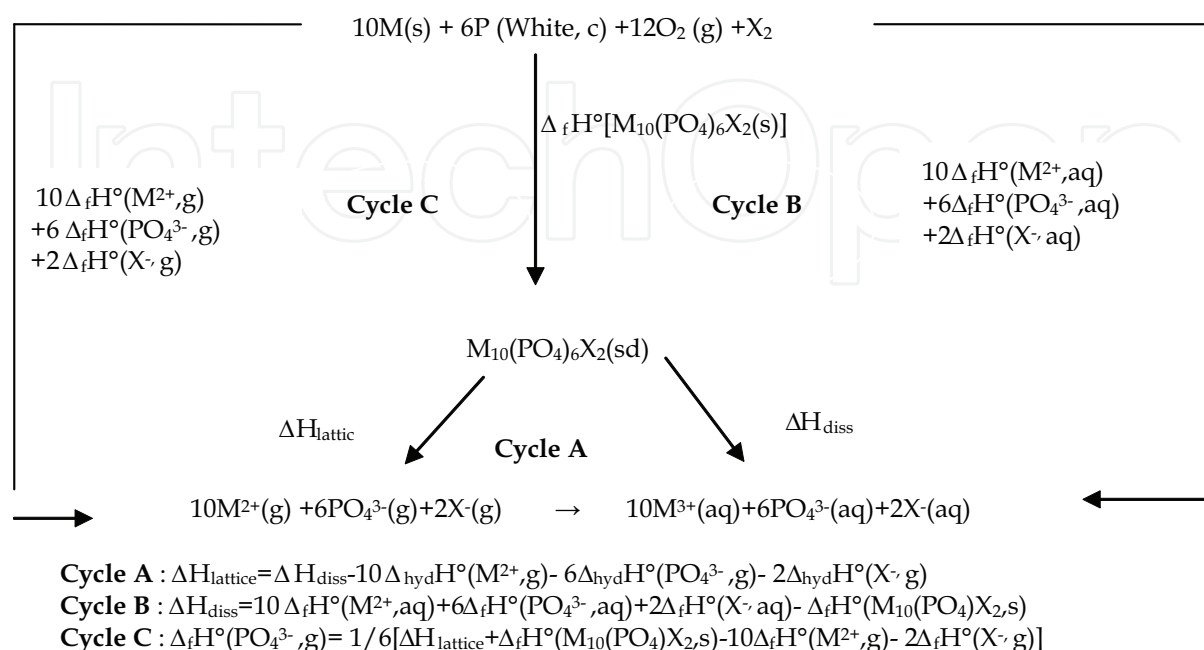


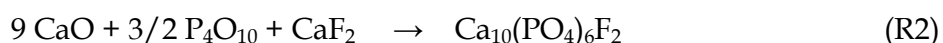
Fig. 2. Thermochemical cycles to derive the lattice enthalpies of the apatites and the formation enthalpy of gaseous PO_4^{3-} at 25°C and to calculate again the dissolution enthalpies (Flora et al., 2004).

4.2 Estimation of standard Gibbs energy of formation

Comparing the stability of similar compounds on the basis of the formation enthalpies supposes the entropy factor be non significant compared to enthalpy. This way of doing remains valid when the enthalpies of formation are significantly different. It also supposes the entropy of formation of the compounds be equal zero. Taking into account the discrepancy between the formation enthalpies of alkali earth apatites and those of cadmium or lead one can compare their stability on the basis of this approach. But when the formation enthalpies are close to each other, entropy factor becomes important and can modify the stability order.

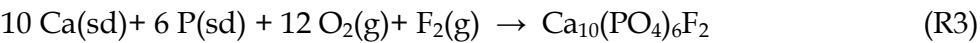
Instead of affecting the zero value to the formation entropy of the compound, an other approach can be developed for better estimating this quantity. This approach consists in involving the compound in a particular reaction for which the formation entropies of reactants and products are tabulated. This leads to determine the upper value of the formation entropy of the compound in concern. By assimilating $\Delta_f S$ be equal to this limit, one can derive a new value of the Gibbs energy.

For example Ca-fluorapatite, CaFap, can be involved in the following reaction:



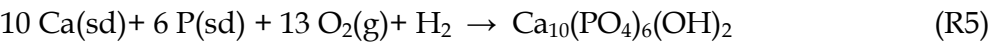
Taking into account the literature data (Handbook, 2006-2007 and JANAF, 1971 for P_4O_{10}), the entropy of this reaction is derived as: $\Delta_{R2}S(T_0) = S^\circ(T_0, CaFap) - 904.6 \text{ J mol}^{-1} \text{ K}^{-1}$, where

T₀ is the standard temperature (298.15 K) and S°(T₀, CaFap) the standard entropy of CaFap at 298.15 K. Entropy of R2 reaction is negative, consequently S°(T₀,Fap) < 904.6 J mol⁻¹ K⁻¹. The formation entropy of Fap is the entropy of the following reaction:



It can be expressed as Δ_fS°(T₀, CaFap) = S°(T₀, CaFap) - 3327,6 J mol⁻¹ K⁻¹. Taking into account the previous inequality one can derive the following inequality as Δ_fS°(T₀, CaFap) < -2423 J mol⁻¹ K⁻¹. So according to this demarche, the upper limit of Δ_fS°(T₀, CaFap) is -2423 J mol⁻¹ K⁻¹. If we assume the formation entropy to be equal this limit, one can derive the standard formation Gibbs energy at T₀ as -12826 kJ mol⁻¹ instead of -13548 kJ mol⁻¹ assuming Δ_fS°(T₀, CaFap) = 0

A similar calculation has been made for Ca-hydroxyapatite, CaHap, considering the following reactions:



and calculation led to -12560 kJ mol⁻¹ for the standard Gibbs energy of formation instead of -13305 kJ mol⁻¹ assuming Δ_fS°(T₀, CaHap) = 0

This approach has been applied to all the apatites listed in table 1 after involving them in reactions having fluorides, oxides, chlorides, H₂O and P₄O₁₀ as reactants. Calculation results are reported in table 2 (Jemal, 2004)

M ₁₀ (PO ₄) ₆ Y ₂	Y = F	Y = OH	Y = Cl
Ca ₁₀ (PO ₄) ₆ Y ₂	-12826	-12560	-12462
Sr ₁₀ (PO ₄) ₆ Y ₂	-12845	-12586	-12477
Ba ₁₀ (PO ₄) ₆ Y ₂	-12834	-12553	-12539
Cd ₁₀ (PO ₄) ₆ Y ₂	-8042	-7872	-7718
Pb ₁₀ (PO ₄) ₆ Y ₂	-7781	-7481	-7457

Table 2. Estimated standard Gibbs energies of formation (in kJ mol⁻¹) of the apatites at 25°C
Table 2 shows that Ca-hydroxyapatite is more stable than Ba-hydroxyapatite, whereas neglecting the entropy factor, table 1, shows the reverse and the difference between their Δ_fG°(T₀) is greater than between their Δ_fH°(T₀). However with this approach one can not explain what was observed experimentally during synthesis of Pb-chlorapatite. This compound has been precipitated in aqueous medium whereas all the other chlorapatites have never been obtained by ‘wet’ method synthesis.

4.3 Thermochemistry of substituted Ca-apatites

Natural apatites are thought to be Ca-apatites in which other metals substitute for Calcium, carbonate or silicate ions for phosphate and carbonate for fluoride or hydroxyl ions. Silicate phosphate apatites are found in high-temperature geological settings such as metamorphic rocks in Oklo (Gabon) and Hoggar (Algeria) or volcanic ejecta. A thermochemical study performed on neodymium silicate Ca-fluorapatites, or britholites, showed a decrease in stability as the amount of couple substitution (Nd,SiO₄) for (Ca,PO₄) increases (Ardhaoui et al., 2006).

X ray diffraction and thermochemical study of substitution of calcium by magnesium in hydroxyl and fluor-apatites showed a limited substitution not exceeding 7% atom in the former and 10 % atom in the latter (Ben Abdelkader et al., 2001). However, substitution by Sr, Cd or Pb in Ca-hydroxy and Ca-fluorapatites is possible over the all range of composition (khattech and Jemal, 1997) (Ben Cherifa and Jemal, 2004) and (Ntahomvukiye et al., 1997) respectively. Thermochemical results showed an increase or decrease in the enthalpy of formation as the substitution increases, depending on the values of the corresponding quantity for the limit apatites. However, heat of dissolution in acid solutions exhibited an extremum at a composition close to that at which Rietveld X ray analysis showed the substituting metal moving preferably from one metallic site to the other in the apatite structure.

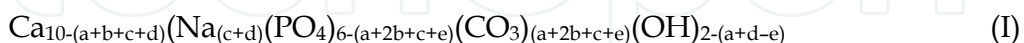
Substitution by CO_3 anion has been widely studied structurally and spectroscopically (Elliott, 1994 and Legeros, 1991). There are two kinds of carbonate apatites. In 'A' type F- or OH^- ions are replaced by CO_3^{2-} . Carbonate ions are centered on the helicoidal senary axis of the network along the tunnels. This substitution is obtained by a solid gas reaction at high temperature, 900°C , under CO_2 gas in very dry conditions. In 'B' type carbonate apatites CO_3^{2-} ions occupy PO_4^{3-} position. There is no ambiguity about the substitution mechanism in A-type carbonate apatites, but for B-type carbonate apatites several mechanisms have been proposed in literature all of them suppose two kinds of CO_3^{2-} in such compounds. These compounds have been subjected to thermal decomposition associated to gas chromatography analysis and the results showed departure of CO_2 in two steps, confirming the presence of two kinds of carbonates in Na free (Khattech and Jemal, 1985 and 1987) and Na bearing (El Feki et al., 1991) carbonate apatites..

De Maeyer and Verbeeck (1993) showed that in Na bearing carbonate apatites the various formulae proposed in literature for B-type hydroxy-compounds derive from the following fundamental mechanisms:

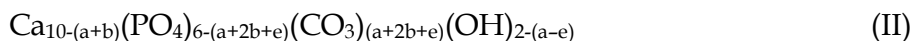
- I) $\text{Ca}^{2+} + \text{PO}_4^{3-} \leftrightarrow \text{V}_{\text{Ca}} + \text{CO}_3^{2-} + \text{VOH}$
- II) $\text{Ca}^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{V}_{\text{Ca}} + 2\text{CO}_3^{2-}$
- III) $\text{Ca}^{2+} + \text{PO}_4^{3-} \leftrightarrow \text{Na}^+ + \text{VOH}$
- IV) $\text{Ca}^{2+} + \text{OH}^- \leftrightarrow \text{Na}^+ + \text{VOH}$
- V) $\text{PO}_4^{3-} \leftrightarrow \text{CO}_3^{2-} + \text{OH}^-$

where V_{Ca} and VOH^- are vacancies of Ca and OH respectively.

Let a, b, c, d, and e the contributions of mechanisms I to V in the composition of the unit cell respectively, the carbonate apatite can be described by the general formula as:



Na bearing carbonate apatites have never been subjected to thermochemical study, but Na free hydroxyapatites have been recently thermochemically studied using the isoperibol calorimeter, and their enthalpies of formation were derived (Bel Hadj Yahia and Jemal, 2010). The general formula of the latter compounds derives from the previous one with 'c' and 'd' equal to zero, this gives the following formula:



Hydroxyapatites having various compositions have been dissolved in a 9% weight nitric acid solution and their dissolution reactions have been combined with other processes in a

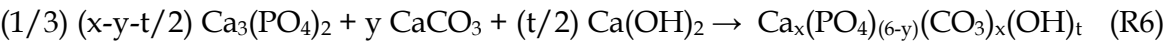
succession of reactions similar to that proposed above for Ca-fluorapatite, in order to get the enthalpies of formation. Table 3 gathers the formulae of these products determined by chemical analysis of Ca, PO₄ and carbonate and their enthalpies of solution and formation. One can notice a decrease of Δ_fH°(T₀) suggesting an increase in stability as CO₃ amount increases until around 1.3 CO₃ and 0.8 OH.

	Δ _{sol} H°T ₀ /kJ mol ⁻¹	Δ _f H°T ₀ /kJ mol ⁻¹
Ca _{9.83} (PO ₄) _{5.82} (CO ₃) _{0.28} (OH) _{1.64}	- 387.76	- 13133.3
Ca _{9.60} (PO ₄) _{5.55} (CO ₃) _{0.53} (OH) _{1.49}	- 397.44	- 12763.3
Ca _{9.35} (PO ₄) _{5.34} (CO ₃) _{0.67} (OH) _{1.34}	- 396.05	- 12352.6
Ca _{9.06} (PO ₄) _{4.95} (CO ₃) _{0.83} (OH) _{1.61}	- 440.99	- 11640.0
Ca _{8.93} (PO ₄) _{4.83} (CO ₃) _{1.06} (OH) _{1.25}	- 421.71	- 11583.0
Ca _{8.82} (PO ₄) _{4.74} (CO ₃) _{1.31} (OH) _{0.80}	- 389.58	- 11618.7
Ca _{8.86} (PO ₄) _{4.65} (CO ₃) _{1.37} (OH) _{1.03}	- 420.20	- 11575.4
Ca _{8.76} (PO ₄) _{4.59} (CO ₃) _{1.44} (OH) _{0.87}	- 400.91	- 11474.1
Ca _{8.68} (PO ₄) _{4.52} (CO ₃) _{1.58} (OH) _{0.64}	- 387.48	- 11443.9
Ca _{8.51} (PO ₄) _{4.41} (CO ₃) _{1.63} (OH) _{0.53}	- 401.27	- 11148.3

Table 3. Standard enthalpies of solution and formation for various B-type carbonate Ca-hydroxyapatites.

Taking into account the existence of only two types of carbonates, among ‘a’, ‘b’ and ‘c’ parameters one has to be nil. Thermochemical results have been treated statistically in order to find which couple of parameters has to be considered in the chemical formula in agreement with experimental results. The mathematical model is based on the linear regression on two independent variables. Test of significance of regression coefficients and analysis of variance showed that the most probable substitutions in this kind of products are the couple substitutions (CO₃,OH) for (PO₄) and (2CO₃,V^{Ca}) for (2PO₄), and so thermochemistry showed that the most probable formula of these compounds is Ca_{10-(a+b)}(PO₄)_{6-(a+2b)}(CO₃)_(a+2b)(OH)_(2-a).

It was interesting to determine the influence of carbonate introduction on the lattice enthalpy. This can be made by comparing the formation enthalpy of the apatite to that of the stoichiometric mixture of solids containing the same entities as in apatite. Let Ca_x(PO₄)_(6-y)(CO₃)_x(OH)_t (with 2x = 18 - y + t) the general formula of the CO₃-apatite, the effect of carbonate is tightly related to the enthalpy of the following reaction:



Enthalpy of R6 reaction (Δ_RH) has been determined from literature for the reactants (Handbook 2006/07 and Ben Abdelkader et al., 1999) and from table 3 for the apatites. Figure 3 shows the variation of Δ_RH over both CO₃ and OH amounts in the apatite lattice. One can notice a maximum around 0.8 CO₃ and 1.6 OH, confirming the presence of two kinds of carbonates and showing the variable effect on the lattice enthalpy depending on the side around the maximum.

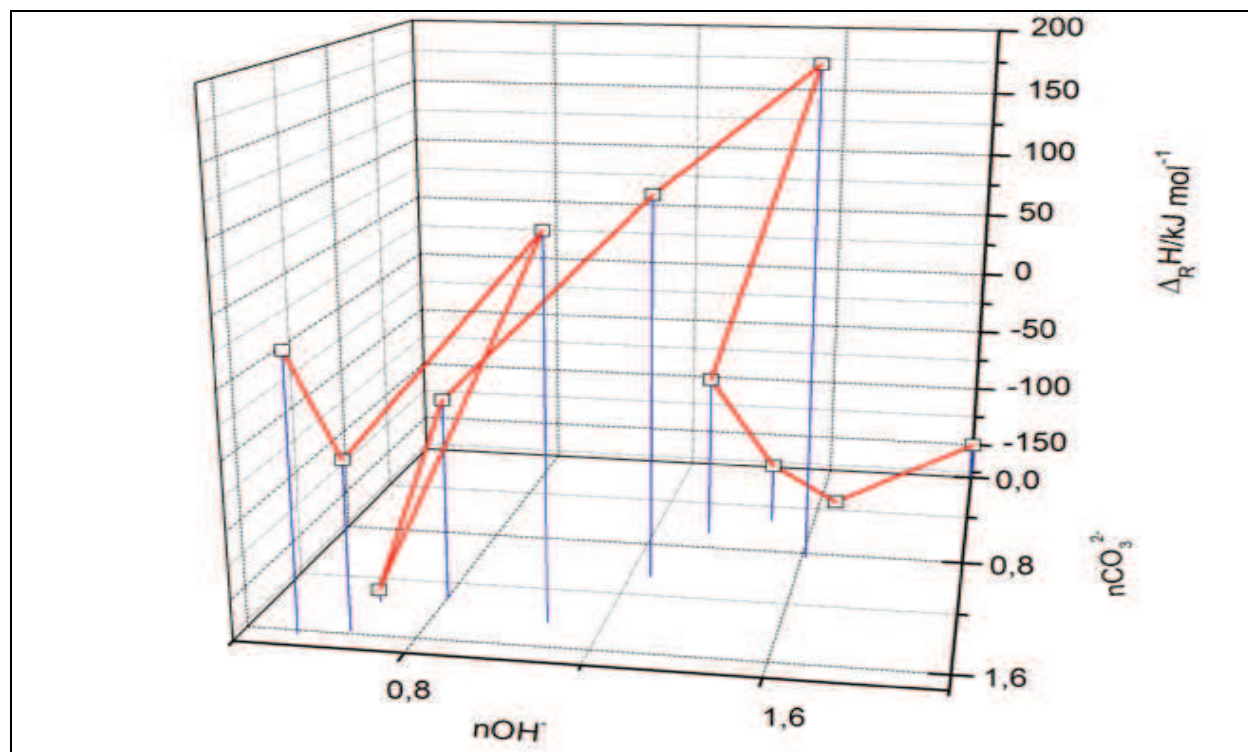


Fig. 3. Variation of enthalpy of reaction R6, $\Delta_R H$, over both CO_3 and OH amounts in B-type CO_3 apatite lattice

5. Microcalorimetry for the attack of phosphates by acid solutions.

Attack of phosphates by acid solutions have been widely studied in literature. Due to the importance of this reaction in manufacturing fertilizers, most of the papers deal with phosphate ores and a few with synthetic phosphates such as fluorapatite, hydroxyapatite or tricalcium phosphate (TCP), monocalcium phosphate monohydrate or other Ca-phosphates. Simulation of the hemihydrate process for H_3PO_4 production has been also developed (Gioia et al., 1977) together with dihydrate process used in Rusaifa (Jordan) pilot plant (Abu-Eishah Samir, I. and Abu-Jabal Nizar, M., 2001). A number of papers developed kinetic models for the attack by H_3PO_4 (Huffman et al., 1957; van der Sluis et al., 1987, Dorozhkin, 1996 and Ben Brahim et al., 1999), HNO_3 (Bayramoglu et al., 1995) or H_2SO_4 (Shakourzadeh et al., 1984 and Sevim et al., 2003). In these works analysis of the solution was mainly used as an experimental technique to follow the evolution of the reaction. Conductance measurements, optical polarization microscopy or isoperibol calorimetry has also been used by some authors. Analysis of the solution proceeds discontinuously and the other techniques do not undergo high sensitivity allowing to follow accurately *in situ* the process over time, particularly in the beginning when the reactions are very rapid.

Microcalorimetry overcomes these drawbacks and gives much more precise information on what is happening *in situ*. Consequently it offers the possibility to propose an attack mechanism showing the intermediate steps which appear during the process and leading to the kinetic model for each of them. This information can be used in order to choose the experimental conditions likely to increase the yield of the attack or to lead to a slurry having particular properties, i.e. containing one or two of the calcium sulfates. This technique has

been used to study the attack of synthetic fluorapatite and a sample of a Tunisian phosphate ore by phosphoric acid or by a mixture of the latter with sulfuric acid.

5.1 Experimental procedure

C-80 SETARAM microcalorimeter is a differential device operating at temperature up to 300°C. It is composed of a thermally isolated jacket provided with two thermopiles each one containing hundreds of thermocouples surrounding a cavity in which a reaction cell is introduced and tightly fixed. The heat effect evolved in the cell is detected by the thermopile then appears as a heat flow on the recorder. The cell is composed of two compartments separated by a cover and aimed at containing separate reactants. The reaction starts by a reversing mechanism putting alternatively the jacket in the returned position at which the cover falls and the reactants are mixed. In order to minimize the stirring effect one of the cells is provided with reactants and the other with an equivalent amount of an 'inert' compound (here is water), and the difference of the signals coming from the cells is recorded over time. Thermograms begin as a horizontal baseline with a heat flow close to zero. Mixing the reactants by the reversing mechanism results in a peak ending by a horizontal line when the process is over. Integration of the peak leads to the heat effect taking into account the calibration constant.

It could be thought that the heat effect appearing in the reaction cell is detected as soon as possible and so the thermogram profile gives a real picture of what is happening during the process, allowing to derive kinetics of the phenomena. This is true only when the process is slow, but when it is fast, the signal produced at the reaction cell, or thermogenesis signal, is delayed and deformed before appearing on the recorder. This difficulty is usually resolved by recording the heat curve, or thermogram, resulting from a phenomenon having a well-known shape profile. Joule effect energy has this particular property. When providing an electrical resistance with a stabilized current during a certain time 't', the heat profile is nil in the beginning, then increases abruptly when switching on and stays constant during 't' time. It falls vertically to zero value when switching off. Because of the thermal resistance of the device, this rectangular shape, or 'échelon' shape, appears differently on recording. However a mathematical treatment of the recorded signal allows to find back the thermogenesis signal. This treatment consists in expressing the recorded signal as a sum of two exponential functions each one having a particular time constant 'τ', as:

$$s(t) = [\tau_1 / (\tau_1 - \tau_2)] [1 - e^{-t/\tau_1}] + [\tau_2 / (\tau_2 - \tau_1)] [1 - e^{-t/\tau_2}] \quad (1)$$

Iteration procedure allows to calculate values of time constants corresponding to tightly superposition of calculated and recorded curves. These values of 'τ' will be then used to calculate back the thermogenesis curve resulting from Joule effect. Entrance signal, or thermogenesis curve, was calculated using the two first derivatives of s(t), ds(t)/dt and ds(t)²/dt², according to the following expression (Dubès et al., 1976):

$$e(t) = s(t) + (\tau_1 - \tau_2) ds(t)/dt + (\tau_1 \tau_2) ds(t)^2/dt^2 \quad (2)$$

The 'échelon' shape of the so calculated curve confirms the validity of the time constant values. It should be noticed that these values depend on the nature of couple of cells introduced in the device (Brahim, 2006). SETARAM provides Joule effect calibration cells very different from the reaction cells, consequently it was necessary to provide the latter with electrical resistances in order to get the time constants values in the same conditions as

for the chemical process (Brahim et al., 2005). Electrical resistance fixed in the reaction cell was connected to stabilized DC supplier in order to deliver a certain amount of Joule effect energy. Figure 4 shows the recorded and calculated, or deconvoluted, signals obtained for a electrical input in the reaction cell, with $\tau_1 = 404$ seconds and $\tau_2 = 30$ seconds. One can notice the large difference between the two signals and the 'échelon' shape of the calculated one.

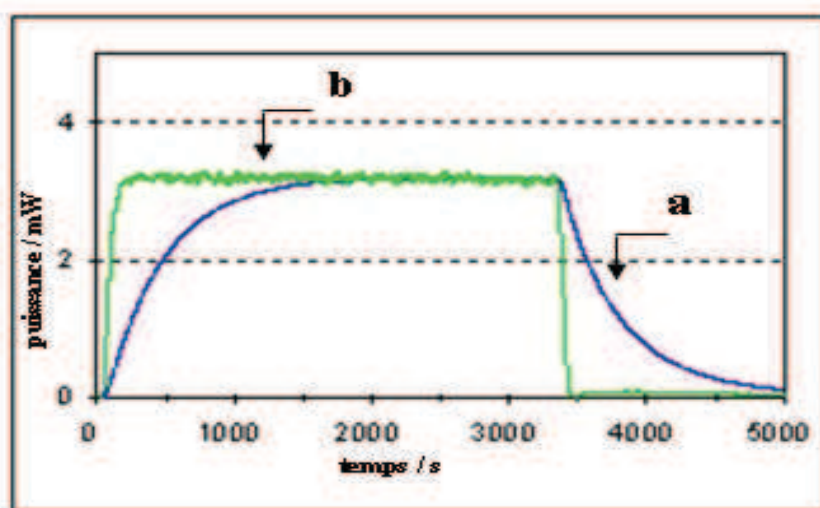


Fig. 4. Recorded (a) and calculated (b) signals for an electrical energy supplied in the reaction cell at 25°C

Time constants determined in that conditions were used to calculate the deconvoluted curves resulting from chemical processes, and the device so provided with electrical resistances has been checked by a key reaction, which is the saponification of ethyl acetate. Thermodynamic and kinetic parameters obtained with this reaction are in good agreement with the published values (Willson et al. 1995).

5.2 Attack of fluorapatite by phosphoric acid solutions

Various amounts of Fap have been dissolved in phosphoric acid solution having 10%, 18% and 30% weight P_2O_5 , and the heat effects were calculated by integration of the peaks whereas the kinetic scheme were determined using the deconvoluted curves.

5.2.1 Thermodynamics

The drawing of the heat effect over Fap mass 'm' is composed of 2 to 3 segments, depending on the acid concentration. Figure 5 shows the graph obtained with the 18% P_2O_5 solution. One can notice the presence of 3 segments corresponding to 'a', 'b' and 'c' domains. In the first one no solid was observed, whereas domains 'b' and 'c' correspond to precipitation of Mono-Calcium Phosphate Monohydrate (MCPM), $Ca(H_2PO_4)_2 \cdot H_2O$, and of a mixture of the latter with Di-Calcium Phosphate Dihydrate (DCPD), $CaHPO_4 \cdot 2H_2O$, respectively. The presence of these compounds has been checked by X ray diffraction analysis performed on the solid precipitated in these domains.

The slope of line 'a' gives the enthalpy of solution of Fap in 18% weight P_2O_5 solution as $\Delta_{sol}H^\circ(T_0) = -171.1 \text{ kJ mol}^{-1}$. Lines 'a' and 'b' intercept at $m = 53.71 \text{ mg}$ for 4.5 mL solution, leading to 0.118 mol L^{-1} for the solubility of MCPD in the acid solution, and the difference between the slopes of lines 'a' and 'b' equals the enthalpy of precipitation of MCPH per unit

mass and leads to $-5.27 \text{ kJ mol}^{-1}$. This value is in good agreement with literature value $-5.0 \pm 0.1 \text{ kJ mol}^{-1}$ (Elasri et al., 1995). Deconvoluted curves obtained from thermograms recorded in 'b' domain reveals two separate peaks corresponding to dissolution of Fap and precipitation of MCPM respectively, whereas crude thermogramm contains a peak and a faint shoulder, Figure 6. In region 'c' deconvolution curve contains 3 overlapping peaks corresponding to the two previously mentioned phenomena and precipitation of DCPD respectively. Similar phenomena have been observed for 10% and 30% weight P_2O_5 solutions (Brahim et al., 2006).

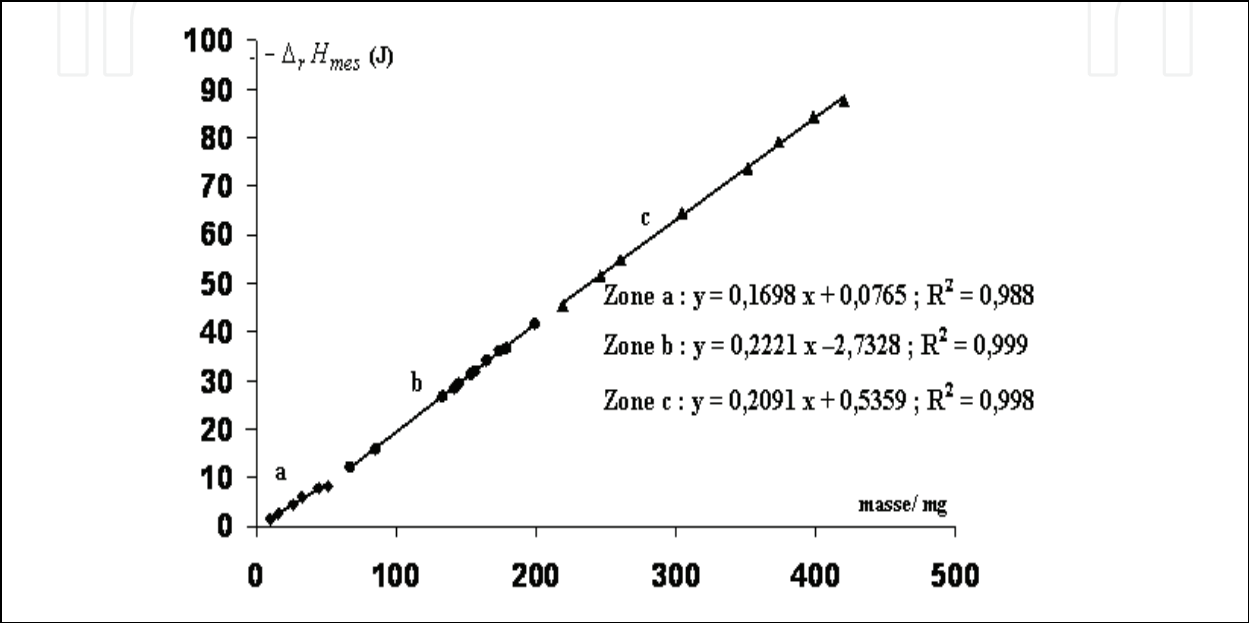


Fig. 5. Heat of solution of Fluorapatite in 18% weight P_2O_5 solution *versus* dissolved mass 'm' at 25°C in 4.5 mL solution

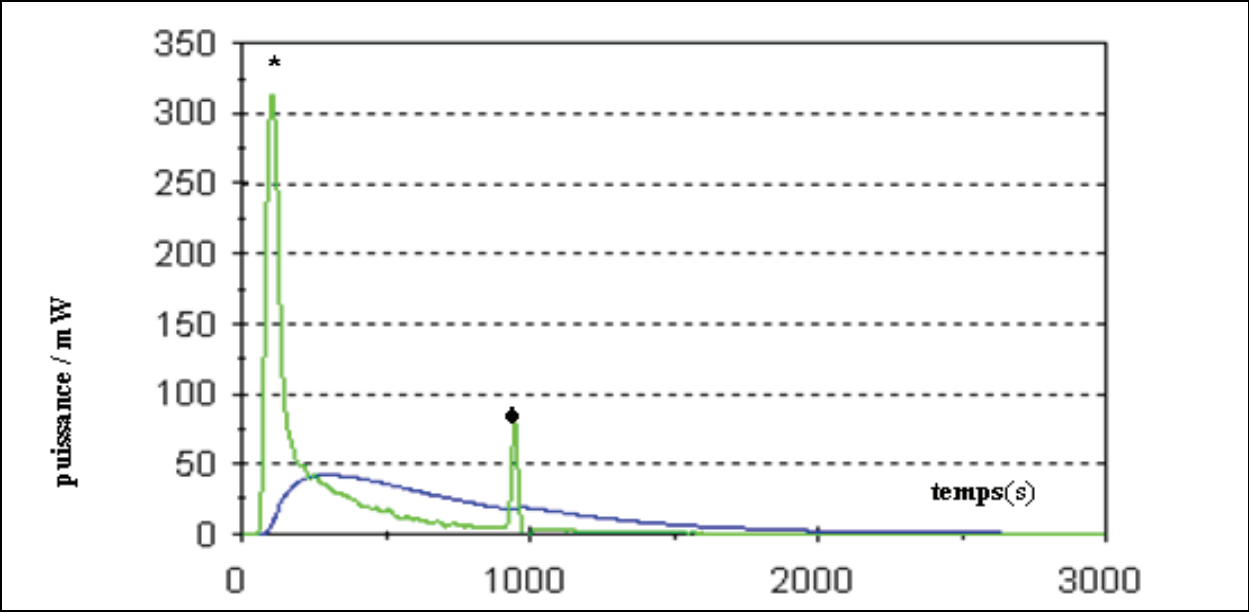


Fig. 6. Crude thermogram (blue) and deconvoluted (green) curves for the attack of Fap with 18% solution

5.2.2 Kinetic schemes

5.2.2.1 Attack by phosphoric acid at 25°C.

Deconvoluted curve gives the more real picture of what is happening during the process, and so it can be used to derive a kinetic model or scheme. The procedure begins by supposing a mathematical model then deriving the corresponding heat flow expression. This expression contains kinetic (order rates and constants) and thermodynamic (enthalpies) parameters. Iteration performed on the heat flow expression allows to find out the best values of parameters leading to the coincidence between calculated and deconvoluted curves. An other criterion of validity of the model consists in comparing the enthalpy deduced from iteration to the experimental value obtained by integrating the thermogram.

As an example let us consider the dissolution of fluorapatite, Fap, (domain 'a' in figure 5). In this domain kinetic models with one step, two opposite or two successive steps have been supposed then the corresponding heat flow expressions were derived, but the coincidence between iterated and deconvoluted curves was obtained only with a two successive reaction model with rate order one for calcium. Here only the latter was considered because of the few amount of Fap compared to that of the acid

In this model Fap (A) reacts with the solution to give an entity (B) which transforms into (C) according to the scheme:



The reaction rates are expressed as : $r_1 = k_1 C(A)$ and $r_2 = k_2 C(B)$ with $C(A)$ and $C(B)$ are the concentrations of A and B species respectively. If the first reaction rate was independent from that of the second , concentration of 'A' species can be expressed as $C(A) = C_0(A) \exp(-k_1 t)$ in which $C_0(A)$ is the initial concentration of A and equals the calcium concentration corresponding to hypothetical complete dissolution of Fap mass in the 4,5mL solution.

B entity appears through reaction 1 and disappears through 2, so its concentration is expressed as:

$$-dC(B)/dt = k_2 C(B) - k_1 C(A)$$

Integrating this expression leads to: $C(B) = \Omega_1 \exp(-k_1 t) + \Omega_2 \exp(-k_2 t)$ in which Ω_1 and Ω_2 are integration constants. Taking account the absence of B species at zero time leads to : $\Omega_1 = -\Omega_2$ and so $C(B)$ is derived as:

$$C(B) = C_0(A) \frac{k_1}{k_1 - k_2} [\exp(-k_2 t) - \exp(-k_1 t)]$$

Mass conservation of matter imposes : $C(A) + C(B) + C(C) = C_0(A)$ and so concentration of C is derived as :

$$C(C) = C_0(A) \left[1 - \frac{k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)}{k_2 - k_1} \right]$$

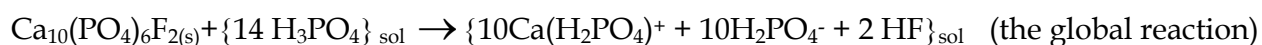
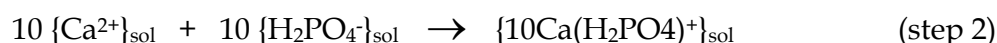
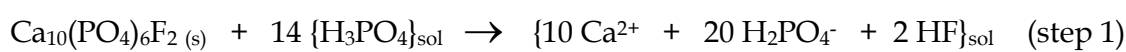
Let q_1 and q_2 the energy amounts resulting from 1 and 2 reactions respectively, these quantities equal $q_1 = [C_o(A) - C(A)]V\Delta_1H$ and $q_2 = C(C) V\Delta_2H$ with V the solution volume and Δ_1H and Δ_2H the molar enthalpies of reactions 1 and 2 respectively. The derivative of the total energy ($q = q_1 + q_2$) is expressed as:

$$\frac{dq}{dt} = \frac{m_A}{M_A} \left[\frac{\Delta_2H k_1 k_2}{k_1 - k_2} (\exp(-k_2 t) - \exp(-k_1 t)) + \Delta_1H k_1 \exp(-k_1 t) \right]$$

in which M_A is the molar weight of Fap and m_A mass initially introduced. This expression gives the variation of heat flow over time according to this model and contains the four unknown parameters k_1 , k_2 , Δ_1H and Δ_2H .

Iteration procedure has been performed on this expression in order to get suitable values of these parameters and the results are shown on figure 7 for 18% and 30% weight P_2O_5 solutions with different mass of dissolved Fap. Dissolution enthalpies of Fap giving the best coincidence for 18% P_2O_5 solution are $\Delta_1H = -182.5 \text{ kJ mol}^{-1}$ and $\Delta_2H = 10.3 \text{ kJ mol}^{-1}$ and the sum $-172.2 \text{ kJ mol}^{-1}$ is close to that determined experimentally by integrating the recorded peak ($-171.0 \pm 2.0 \text{ kJ mol}^{-1}$). For 30% P_2O_5 solution iteration enthalpies equal -158.3 and 10.3 kJ mol^{-1} respectively and their sum -148.0 is also close to the experimental value ($-147.0 \pm 1.7 \text{ kJ mol}^{-1}$).

So dissolution of Fap in phosphoric acid solution likely occurs in two successive steps, the first one could be a simple dissolution and the second the formation of the $[Ca(H_2PO_4)]^+$ complex ion in the dissolved state, according to the chemical scheme :



$[Ca(H_2PO_4)]^+$ complex ion has been reported in literature and its stability constant has been determined at 25°C as 5.1.

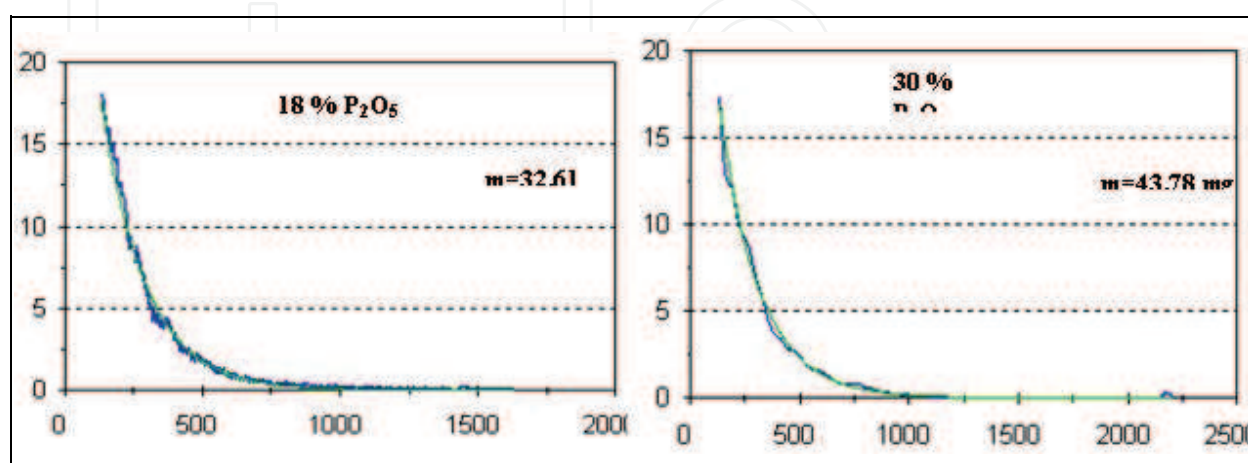


Fig. 7. Examples of coincidence between iterated (green) and deconvoluted (blue) curves for dissolution of Fap in 18% and 30% weight P_2O_5 solutions at 25°C .

In that hypothesis, the second peak corresponds to precipitation of MCPM according to the reaction:



A kinetic scheme has been also established for this process by considering the second peak in the deconvoluted curve on figure 6 as corresponding to only one reaction:

Let $C([\text{Ca}(\text{H}_2\text{PO}_4)^+])$ the concentration of $[\text{Ca}(\text{H}_2\text{PO}_4)^+]$ in the solution at t time, because of the relatively high amounts of H_2PO_4^- and H_2O , the precipitation rate of MCPM is expressed taking into account only the concentration of calcium, as:

$$r = -dC([\text{Ca}(\text{H}_2\text{PO}_4)^+]) / dt = k [C([\text{Ca}(\text{H}_2\text{PO}_4)^+])]^n$$

with k and n the order and constant rate. $[\text{Ca}(\text{H}_2\text{PO}_4)^+]$ amount at time t equals the difference between its amount at initial time and that of the reacting quantity and so:

$$C([\text{Ca}(\text{H}_2\text{PO}_4)^+]) = C_0([\text{Ca}(\text{H}_2\text{PO}_4)^+]) - C_{\text{react}}([\text{Ca}(\text{H}_2\text{PO}_4)^+])$$

The heat amount evolved at time t is expressed as : $q = C_{\text{react}}([\text{Ca}(\text{H}_2\text{PO}_4)^+])V\Delta_rH$ and the total heat is $Q = C_0([\text{Ca}(\text{H}_2\text{PO}_4)^+])V\Delta_rH$, with V the total volume of solution and Δ_rH the molar enthalpy of the reaction.

The heat flow is then derived as:

$$\frac{dq}{dt} = k(V\Delta_rH)^{1-n}(Q-q)^n$$

Iteration has been performed for various amounts of Fap dissolved in 18 and 30% weight P_2O_5 solutions. An example of coincidence between the calculated and deconvoluted curves of the second peak is shown in figure 8. Iteration values of ' n ' order, ' k ' constant and ' Δ_rH ' enthalpy are in the ranges: [0.48; 0.52]; [3.10^{-3} ; 16.10^{-3}] and [-5.14; -5.16]/kJ mol⁻¹, respectively.

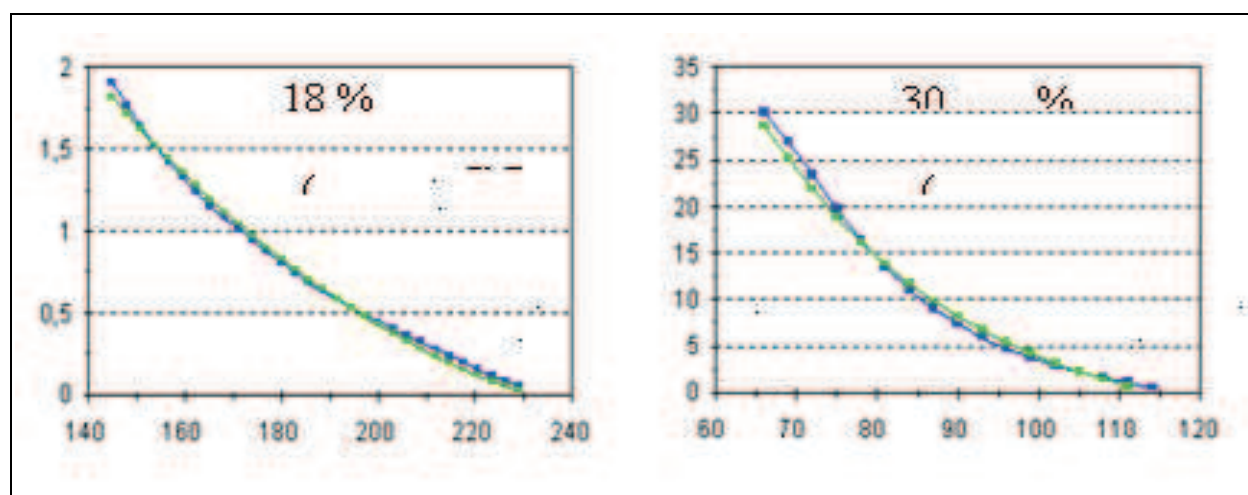


Fig. 8. Examples of coincidence between calculated (blue) and deconvoluted (green) curves for precipitation of Mono-Calcium Phosphate Monohydrate from the solution resulting from dissolution of fluorapatites at 25°C.

' $\Delta_r H^\circ$ ' value agrees with the experimental one obtained by dissolving a commercial sample of MCPM (-5.2 kJ mol^{-1}) and with the values reported in the thermodynamics section § 5.2.1.

5.2.2.2 Attack by phosphoric acid at higher temperatures.

Amounts of Fap close to 30 mg have been attacked by the acid solution at temperatures up to 65°C . Figure 9 shows the molar global enthalpy as a function of temperature. One can notice a particular behavior which can not be explained by the variation of reaction enthalpy according to Kirchhoff relationship, that is:

$$\Delta_r H^\circ(T) = \Delta_r H^\circ(T_0) + \Delta_r C_P^\circ(T - T_0) ; \text{ supposing } \Delta_r C_P^\circ \text{ constant.}$$

This relation leads a smooth variation in the $[T_0 - T]$ temperature range. The presence of an extremum in the molar enthalpy curve suggests a mechanism modification around 45°C .

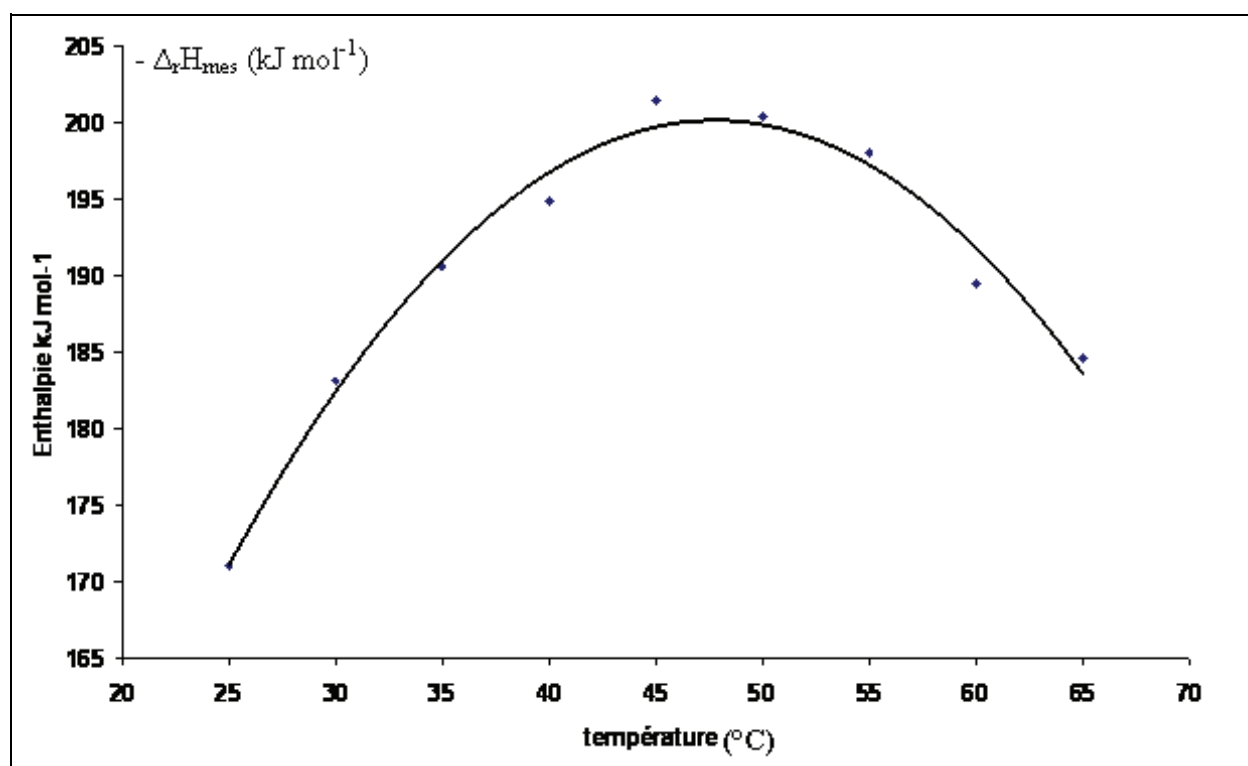


Fig. 9. Molar global enthalpy of the attack of fluorapatite by the acid mixture *versus* temperature.

The kinetic model based on two successive reactions seems to be suitable until 40°C giving a good coincidence between the deconvoluted and calculated curves and enthalpy values not exceeding 2% the experimental ones. For higher temperature the coincidence was very bad and the one step model seems to be much more suitable. This model gave values of the order rate and reaction enthalpy in the ranges $[0.98 ; 1.15]$ and $[-185.5 ; -202.2] \text{ kJ mol}^{-1}$. Experimental values of the latter are in the range $[-184.6 ; -200.4] \text{ kJ mol}^{-1}$. An activation energy of the process in that range of temperature was calculated as 101 kJ mol^{-1} (Brahim, K. et al., 2008), whereas in the lower temperature range the activation energy for the first step was around 20 kJ mol^{-1} . The process seems to be governed by a diffusion phenomenon at lower temperature and by a chemical reaction when temperature increases.

5.3 Attack by the mixture of phosphoric and sulphuric acids.

Phosphoric acid is produced industrially by mixing the ore with sulphuric acid or with recycled phosphoric acid solution together with sulphuric acid. Attack by the acid mixture is supposed to begin by the dissolution of the ore in phosphoric acid. Then production of phosphoric acid occurs together with precipitation of phosphogypsum. This scheme has never been evidenced.

In order to model this attack, microcalorimetry has been used to follow at temperature up to 65°C the attack of various amounts of fluorapatite by a solution obtained by mixing 80% volume of a 20% weight P_2O_5 solution with 20% volume of a 98% weight H_2SO_4 solution.

At 25°C the heat effect resulting from the attack of various masses of Fap, 'm' (25 to 115 mg) by 4.5 ml solution is represented as a straight line the slope of which leads to -407.2 kJ mol⁻¹ Fap.

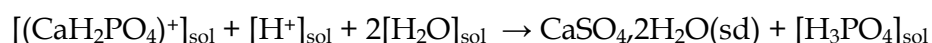
Various kinetic models with one or two steps have been supposed for the process, but no one led to an overlapping between the calculated and deconvoluted curves. The whole phenomenon seems to be more complex. Consequently, Avrami mathematical model has been applied in order to determine the number of steps in the process. In this model the transformed fraction 'x' of a reactant is related to time 't' by the following relation $-\ln(1-x) = kt^n$ with k and n as constants. At the origin this model has been developed theoretically in order to determine the number of directions crystallization occurs (uni, bi or tridimensional crystallization). It has then been extended to chemical transformations and allowed to determine the number of the major reactions involving in a chemical process.

According to this model, $\ln[-\ln(1-x)]$ as a function of $\ln t$ has a straight line shape in a domain corresponding to one predominant phenomenon, and so the drawing of that function for the whole process gives the number of successive phenomena it contains. This number equals that of straight lines existing on the graph (Avrami graph).

In the present case, the transformed fraction of Fap at 't' time was calculated by dividing the heat evolved until t time, q, by the total heat amount, Q. This ratio equals that of the corresponding surface areas. Figure 10 shows the Avrami curves for various masses of Fap attacked by 4.5 mL solution during 8 hours under shaking. One can notice two straight lines each one corresponding to a predominant reaction. Supposing the first step be the dissolution of Fap and the second the precipitation of gypsum, one can deduce the time at which the latter begins (≈ 55 seconds).

It should be noticed that because of the low diffusion process across the gypsum shell around the grains, the attack by the acid mixture doesn't finish even after 8 hours maturation time under shaking and the calorimeter signal didn't reach the horizontal line after several hours. However, for comparison this time has been chosen for the experiments above.

Suppose the dissolution of Fap giving $[(CaH_2PO_4)^+]$ ions, the second step corresponds to the following reaction:



A kinetic scheme with only one step starting at 55 seconds seemed to be the most suitable for this reaction, with the same mathematical formalism as for precipitation of MCPM § 5.2.2.1. Calculation for various amounts of Fap led to the best coincidence with values of kinetic and thermodynamic parameters in the ranges [1.98 ; 2], [0.1039 ; 0.1062] and [-229.0 ; 231.2] kJ mol⁻¹ for the order, the constant and the molar enthalpy respectively (Antar et al., 2006). The order rate of calcium is in good agreement with value 2 reported in literature.

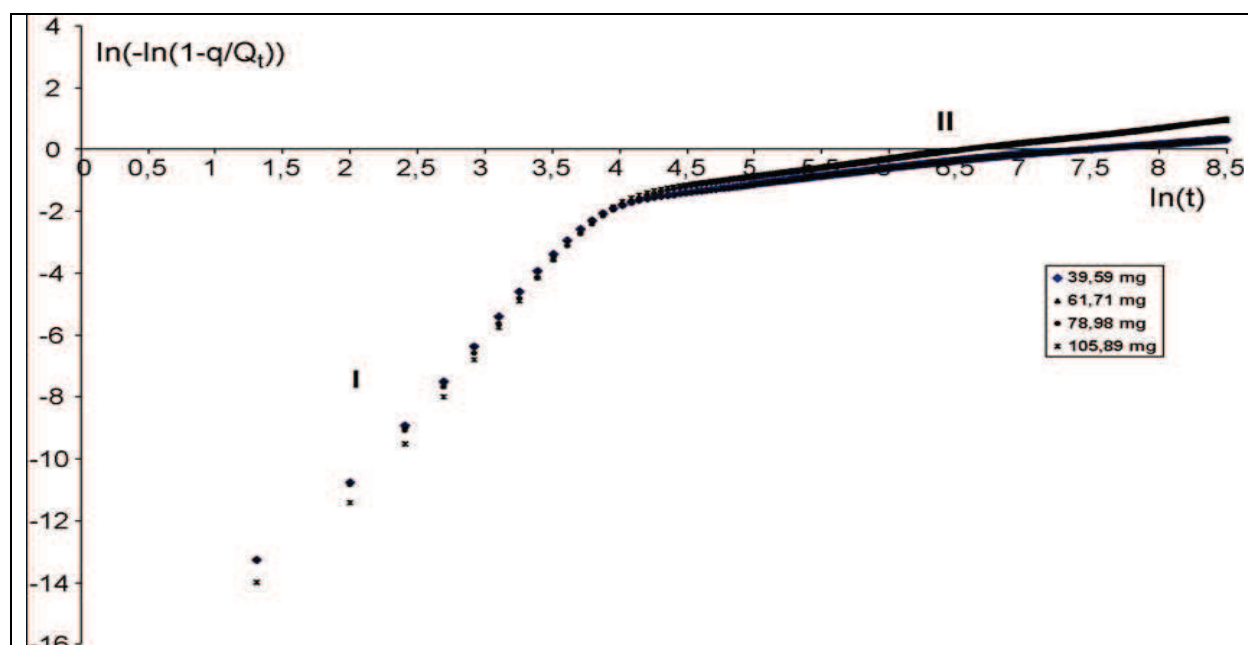


Fig. 10. Avrami graph for various masses of Fluorapatite attacked by 4.5 mL of mixture acid solution at 25°C

Experimental determination of the heat effect of the reaction above has been performed by determining the difference between the energy resulting from the addition of the mixture acid solution to 'pure' H_3PO_4 solution or to a H_3PO_4 solution previously provided with Fap. The results gave $-224.5 \text{ kJ mol}^{-1}$ Fap, which differs from the iteration value by 2.3% (Antar, 2007), confirming the attribution of the step appearing at 55 seconds to gypsum precipitation. The presence of two steps in the whole process appears on the Avrami curves and not on the crude and deconvoluted curves which contain only one peak at 25°C.

Adding the mean value of the gypsum precipitation enthalpy (-230 kJ mol^{-1}) to that resulting from dissolution of Fap in 18% weight P_2O_5 solution $-171.6 \text{ kJ mol}^{-1}$ (mean value) leads to $-401.6 \text{ kJ mol}^{-1}$ which differs from that resulting from the attack of Fap with the acid mixture (-407.0) by 1.3 %, confirming the two steps in the whole process.

When the attack temperature increases, a second peak appears and overlaps partly the first one till 55°C when they separate. X ray diffraction performed on the solid present between the peaks and at the end of the process reveals the transitory formation of calcium sulphate hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, (HH), which transforms into dihydrate (DH) or gypsum when the time elapses. That transformation lasts about 20 hours at 55°C. Figure 11 shows an example of crude and deconvoluted curves obtained at 55°C, together with a zooming in the region of each peak.

5.4 Transformation of Ca-sulfate hemihydrate into dihydrate at 55°C

Various amounts 'm' of Fap have been attacked by the acid mixture at 55°C, and the graphs representing the heat effects over 'm' gave -27.9 kJ and -13.1 kJ per mol of HH and DH respectively.

A kinetic model with two successive Ca-order one reactions was developed for the first peak and gave the better coincidence of the calculated and deconvoluted curves. The iteration enthalpy mean values are -150.3 and -120.3 kJ per Fap mole. Their sum (-270.6) differs from the peak integration one (-278.7) by about 3%. Complementary experiments allowed to

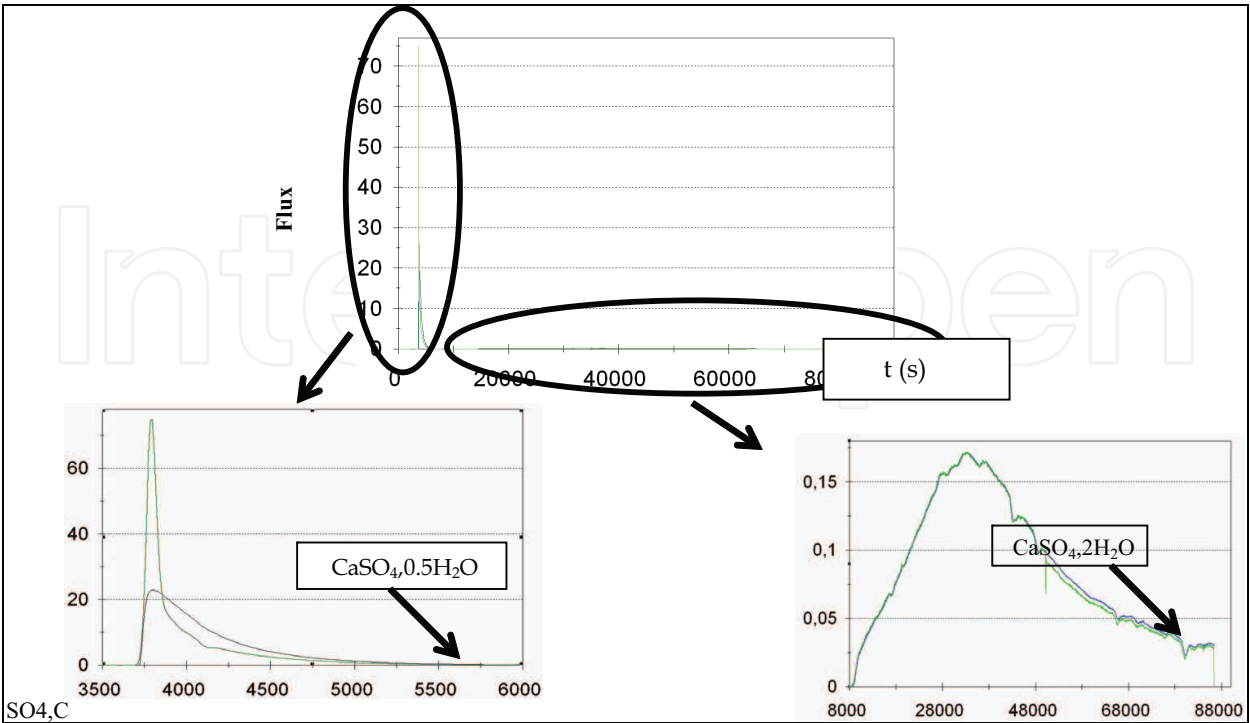
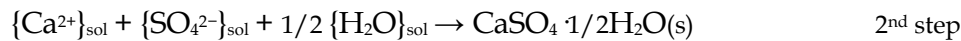
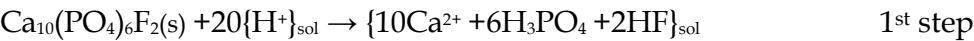


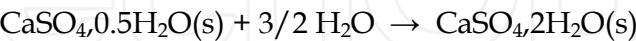
Fig. 11. Deconvoluted (green) and crude (blue) curves for the attack of fluorapatite by phosphoric and sulfuric acid mixture at 55°C

attribute the first step in the first peak to dissolution of Fap and neutralization of H_2PO_4^- into H_3PO_4 , and the second step to precipitation of Ca-sulfate hemihydrate, (HH), according to the following reactions:

For the first peak:



with mean iteration enthalpy values as -150.3 kJ and -120.3 kJ per mole of Fap. This corresponds to -15.0 and --12.0 kJ per mole of Ca-sulfate, respectively. and for the second peak:



A kinetic model based on a dissolution/precipitation process has been developed for the second peak, in which dissolution rate of HH, r_{dis} , is proportional to under saturation ($C_e - [\text{Ca}]$) where C_e is the Ca concentration corresponding to solubility of HH, whereas precipitation rate of DH, r_{pp} , is of order rate 2 for Ca concentration, and so:

$$r_{\text{dis}} = k_1(C_e - [\text{Ca}^{2+}]) \text{ and } r_{\text{pp}} = k_2 [\text{Ca}^{2+}]^2$$

where k_1 and k_2 are constant rate.

The global rate is controlled by the Ca^{2+} concentration, so: $d[\text{Ca}^{2+}]/dt = r_{\text{dis}} - r_{\text{pp}}$

$$d[\text{Ca}^{2+}]/dt = k_1(C_e - [\text{Ca}^{2+}]) - k_2 [\text{Ca}^{2+}]^2$$

$$\text{giving } d[\text{Ca}^{2+}]/dt + k_2[\text{Ca}^{2+}]^2 + k_1[\text{Ca}^{2+}] = k_1\text{Ce}$$

Usual methods for resolution did not make it possible to solve this equation. But Maple 6 software gave the two following solutions:

$$[\text{Ca}^{2+}] = [1/2k_2][-k_1 + C_1\text{th}\{C_1t/2 + \ln C_2\}]$$

and

$$[\text{Ca}^{2+}] = [1/2k_2][-k_1 + C_1\text{th}\{C_1t/2 + \ln(-C_2)\}]$$

with C_1 and C_2 two constants depending both on k_1 , k_2 and Ce .

$$C_1 = [4k_1\text{Ce}k_2 + k_1^2]^{1/2} \text{ and } C_2 = [1/2k_2\text{Ce}][4k_1C_1 - 2k_1^2 - 8k_1k_2\text{Ce} - 4C_1\text{Ce}k_2 - 4\text{Ce}^2k_2^2]^{1/2}$$

The adopted solution is given by the first relation because C_2 constant should have a positive value.

Let Q_1 and Q_2 denote the heat quantities released by hemihydrate dissolution and dihydrate precipitation reactions respectively. Variation of each of these quantities is proportional to the corresponding reaction rate as:

$$dQ_1/dt = V\Delta_{\text{dis}}Hk_1(\text{Ce} - [\text{Ca}^{2+}]) \text{ and } dQ_2/dt = V\Delta_{\text{pp}}Hk_2[\text{Ca}^{2+}]^2$$

with $\Delta_{\text{dis}}H$ and $\Delta_{\text{pp}}H$ the molar enthalpies of dissolution of HH and precipitation of DH, respectively.

The total energy is $Q = Q_1 + Q_2$ and its variation is expressed as:

$$dQ/dt = V\Delta_{\text{dis}}Hk_1(\text{Ce} - [\text{Ca}^{2+}]) + V\Delta_{\text{pp}}Hk_2[\text{Ca}^{2+}]^2$$

The final heat flow expression is expressed as:

$$dQ/dt = V\Delta_{\text{dis}}Hk_1[\text{Ce} - (1/2k_2)(-k_1 + C_1\text{th}\{C_1t/2 + \ln C_2\})] + V\Delta_{\text{pp}}Hk_2[(1/2k_2)(-k_1 + C_1\text{th}\{C_1t/2 + \ln C_2\})]^2$$

Iteration on this expression has been performed in order to get the suitable values of the 6 parameters, $\Delta_{\text{dis}}H$, $\Delta_{\text{pp}}H$, k_1 , k_2 , Ce and C_2 , giving the better coincidence between calculated and recorded curves corresponding to the second peak. C_2 parameter was included because of the complexity of its expression. Due to the low rate of the transformation deconvoluted and recorded curve overlap as shown on figure 11. Figure 12 gives an example of calculated and recorded curves obtained for 39.41 mg Fap. For the other masses of Fap, coincidence is similar and the whole iteration values of k_1 , k_2 , $\Delta_{\text{dis}}H$, $\Delta_{\text{pp}}H$, Ce and C_2 pertain to the intervals: $[4.15 \times 10^{-5}; 5.00 \times 10^{-5} \text{ s}^{-1}]$, $[1.45 \times 10^{-3}; 1.99 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}]$, $[11.90; 12.30 \text{ kJ mol}^{-1}]$, $[-25.10; -24.90 \text{ kJ mol}^{-1}]$, $[3.12 \times 10^{-4}; 3.27 \times 10^{-4} \text{ mol L}^{-1}]$ and $[31.01; 59.33]$, respectively (Antar and Jemal, 2007). It can be noticed that the mean iteration value of $\Delta_{\text{dis}}H$ of HH (+12.10 kJ mol⁻¹) is very close to the opposite of the previous iteration enthalpy of precipitation of hemihydrate (-12.0 kJ per mole of Ca-sulfate).

5.5 Attack of a phosphate ore.

A natural phosphate (NP) ore sample containing 23.6 % P_2O_5 , 38.4 % CaO and 15.1 % calcite has been attacked by the 20% weight P_2O_5 solution and by the mixture of acids at different temperatures.

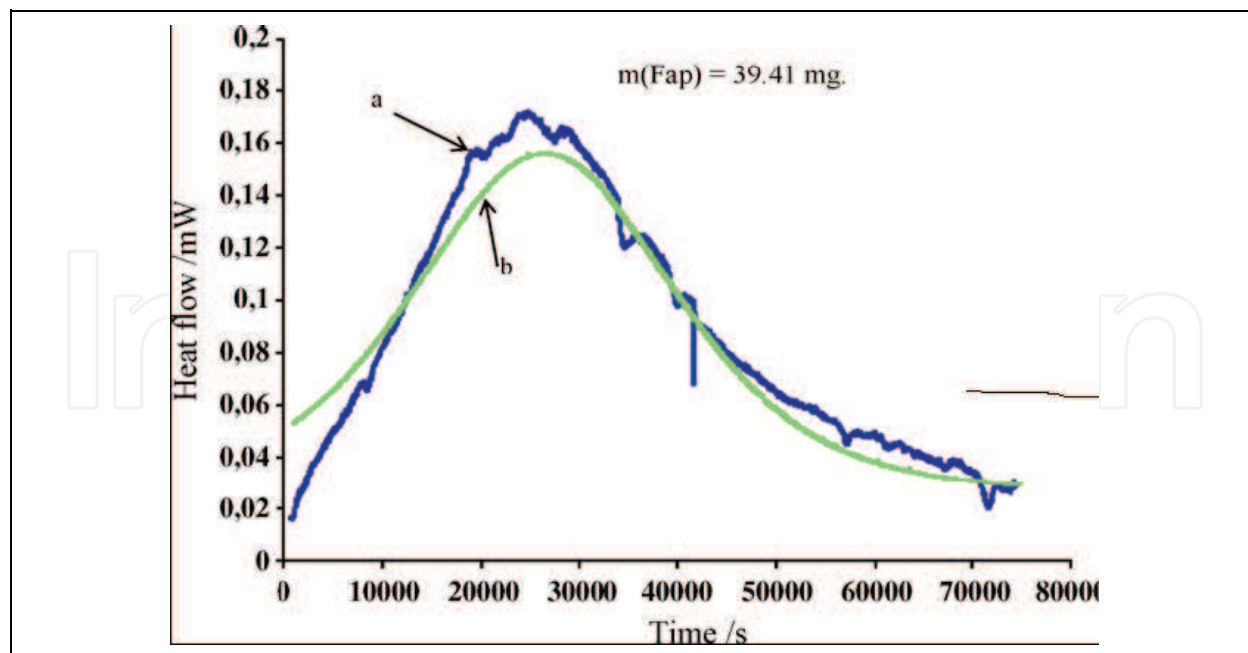


Fig. 12. calculated (b) and recorded (a) curves for the transformation of Ca-sulfate hemihydrate into dehydrate at 55°C (second peak).

The drawing of the heat evolved by attacking at 25°C few amounts of a sample with a granulometry $\leq 500 \mu\text{m}$ in 4.5 mL phosphoric acid solution showed only dissolution with -233.6 J per gram ore. A very close value has been obtained with a sample obtained by grinding the former in an agate mortar. Attack of greater amounts in the same conditions led to an Avrami curve with two successive phenomena corresponding to dissolution and precipitation of Di-Calcium Phosphate Dihydrate, DCPD, the latter starting at about 2.5 minutes (Brahim, 2006). DCPD has been identified by X ray diffraction performed on the isolated solid.

Attack by the acid mixture was very long and gave a two overlapped peaks signal which didn't become horizontal even after several hours. After 8 hours maturation time under shaking the heat effect was -161.5 J g^{-1} for the $\leq 500 \mu\text{m}$ sample and -305.5 J g^{-1} for the grinded one, confirming the dependence of the yield of the process on the grain size of the ore. As for Fap, complementary experiments consisting in adding the acid mixture to a H_3PO_4 and to a $\text{H}_3\text{PO}_4/\text{NP}$ solutions allowed to deduce the enthalpy value for complete NP attack as -377.6 J g^{-1} , and so after 8 hours maturation time only 43% and 81% of non grinded and grinded samples reacted. X ray diffraction performed on the solids isolated after 8 hours reaction time showed a mixture of Ca-sulphate hemihydrate and dehydrate. As with Fap, reaction of NP with the acid mixture leads to HH which transforms into DH. This was observed for NP at 25°C whereas for Fap for higher temperatures. The presence of impurities in the solid results in lowering the temperature of transitory formation of HH.

Figure 13 shows what was obtained by attacking various amounts of NP at 25°C by 4.5 mL of the acid mixture solution. It should be noticed that the peaks overlap more when the amount of NP increases. Avrami curves show the second peak starting at around 100 seconds for a solid mass until about 100 mg and started earlier when the solid amount increases. This is in agreement with literature data concerning the decrease of germination time when the over saturation increases.

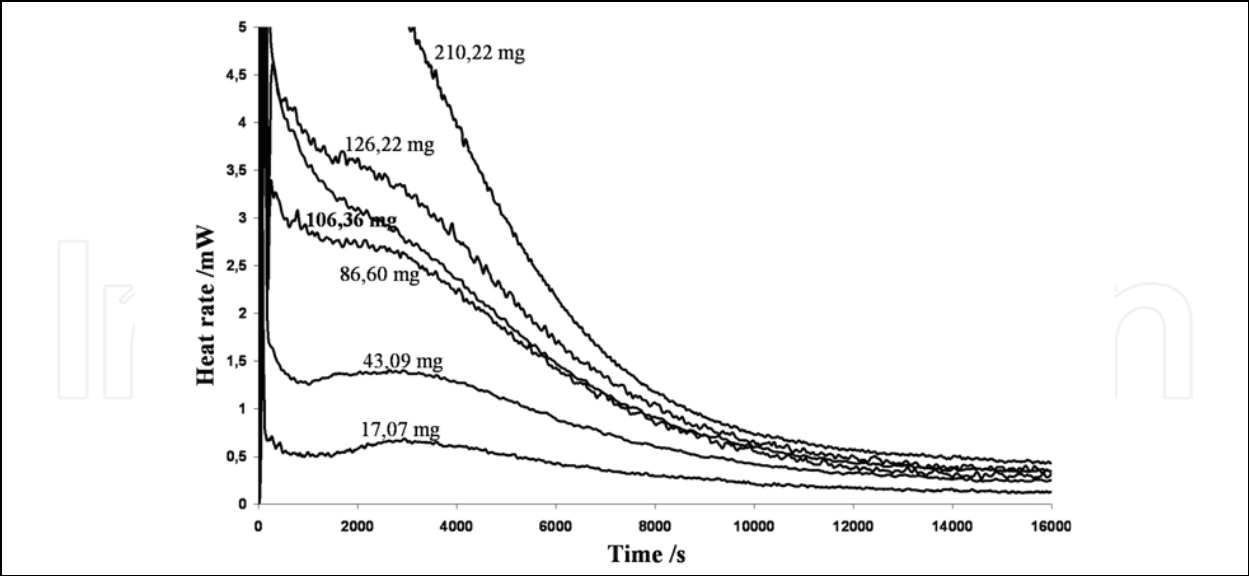


Fig. 13. Thermograms obtained by attacking various amounts of NP by phosphoric and sulfuric acid mixture at 25°C.

When the attack temperature increases, the second peak departs from the former but they didn't separate and the signal remains with only two peaks till 55°C where a third peak appeared at about 18.5 hours and didn't finish even after 45 hours under shaking, Figure 14 shows a crude thermogramm recorded during about 33 hours with 32.63 mg of NP attacked with 4.5 mL of acid mixture solution at 55°C (Antar and Jemal, 2008). X ray analysis performed on the solid isolated at different times reveals that the first peak corresponds to dissolution of the ore and precipitation of a mixture of HH and AH (anhydrous Ca-sulfate), the second peak to transformation of HH into DH and the third to transformation of AH into DH.

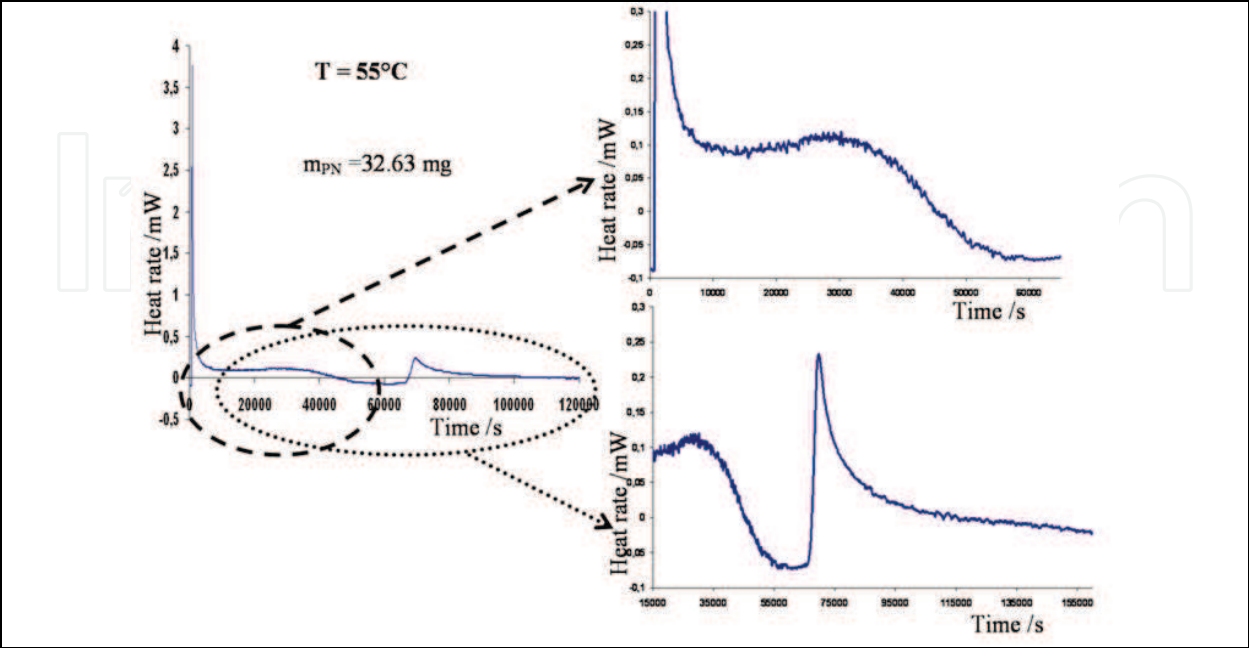


Fig. 14. Thermogram recorded with NP attacked with acid mixture at 55°C

6. Conclusion

Isoperibol dissolution calorimetry allowed to determine not only the solution enthalpies but also other important quantities such as the enthalpies of formation or mixing. These quantities are tightly related to lattice energy of the compounds and can be used to calculate the enthalpies of the reaction in which the compounds are involved. Dissolution enthalpy is also useful to determine the solubility of a compound at any temperature from only one experimental solubility value. Experimentation is very easy but the technique has its own limits.

Microcalorimetry is more sophisticated and sensitive and can give information on both thermodynamics and kinetics of the processes. Its application to transformations of phosphates reveals phenomena which have not been previously seen with other techniques. But for a rapid process, the recorded curve doesn't give a real image of what is happening in the reacting medium. Consequently, deconvolution procedure is necessary to find out the thermogenesis curve, however for more precise determination, the time constants of the device have to be determined in the same conditions as for the chemical process. This is possible after suitable modifications operated on the device.

As opposed to other techniques, kinetic models deduced from microcalorimetric results can be checked not only mathematically but also by comparing the heat effect resulting from mathematical model to the experimental one. This represents an additional criterion for the validity of the model. However the procedure is applicable for a one step process whatever is the order rate, provided it affects only one reactant concentration, but for a two step process the procedure is limited to low order rate kinetic equations, otherwise integration becomes impossible and the heat flow expression can't be derived.

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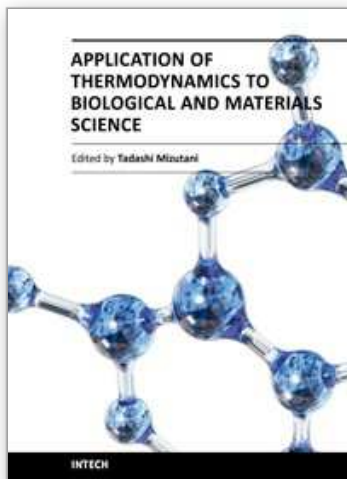
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