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Thermochemical and kinetic studies of the acid attack of “B” type carbonate fluorapatites at different temperatures (25–55)°C

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ABSTRACT

The thermochemical and kinetic study of the attack of “B” type carbonate fluorapatites (B-CO_3-Fap) by a (19% w/w P_2O_5) acid solution was performed using microcalorimetry at a temperature range between 25 and 55 °C and a pH 0.6. The results were processed iteratively in order to get the kinetic constant and the enthalpy of dissolution reaction. The rise in temperature leads to an increase in the apparent rate constant and an increase in the enthalpy of dissolution between (−200 and −140 kJ mol^{-1}) with an order of reaction close to 2. Increasing the amount of carbonate in B-CO_3-Fap generates a decrease in the activation energy 16–8 kJ mol^{-1} suggesting that the dissolution reaction could be controlled by a diffusion phenomenon.

1. Introduction

Sedimentary phosphates are apatite minerals with a complex chemical composition. They derive from fluorapatite ($Ca_{10}(PO_4)_6F_2$) by various substitutions. Carbonate ions can substitute PO_4^{3-} or F^- leading to “B” or “A” type carbonate apatite respectively. Sedimentary phosphates belong to the former type of apatites.

Reaction of phosphate apatites with acid solutions is at the basis of the wet manufacturing process of phosphoric acid. Several studies on the dissolution kinetics and mechanisms of natural apatite in water, buffer solutions or acidic media have been undertaken [1,2]. Sevim et al. [3] dissolved Turkish minerals phosphate in sulfuric acid and found that the reaction rate depends on temperature, particle size, and solid-to-liquid ratio. However, the reaction rate seems to decrease with increasing temperature when the attack of a Turkish mineral phosphate by HCl/HOCl solution [4] or sulfuric acid solution [5] is over 40 °C. Vaimakis et al. [6] found that during the dissolution process of phosphate ores originated from Epirus–Greece area, only the calcite species were mainly dissolved, whereas almost all of the francolite remained in the solid phase.

As the attack of natural phosphates is controversial, some authors have used synthetic apatites. Brahim et al. showed that the digestion reaction of fluorapatite (Fap) by phosphoric acid occurred in two steps and the temperature variation induced a change in mechanism [7]. This result was also found by Antar et al. during the attack of the Fap by mixtures of sulfuric and phosphoric acids [8]. A study performed on the Tunisian mineral phosphate (from Gafsa) at different temperatures (25–90 °C) showed that the attack reaction is rapid with increasing temperature [9].

In a previous work devoted to the thermochemical aspects of the dissolution at 25 °C of synthetic “B” type carbonate fluorapatites at various solid/liquid ratios [10], we showed that only dissolution occurred at low values of that ratio. Furthermore, increasing the ratio led to precipitation of CaF_2 or to a mixture of the latter with monocalcium phosphate monohydrate ($Ca(H_2PO_4)_2{\cdot}H_2O$).

This paper deals with the thermochemical and kinetic aspect of the attack of “B” type carbonate fluorapatites with phosphoric acid solution which composition is close to what is used in industry (19% w/w P_2O_5) at different temperatures (25–55 °C).

2. Experimental

2.1. Synthesis of the apatites

The “B” type carbonate fluorapatites (B-CO_3-Fap) have been synthesized with different amount of carbonate, using the “reverse” procedure [11–17]. This method consists in adding drop by drop a “B” solution containing ammonium phosphate (0.016 M), ammonium fluoride (0.04 M) and ammonium carbonate ($0.5 < [CO_3^{2-}]/[PO_4^{3-}] < 6$) in a boiling “A” solution containing the calcium nitrate (0.04 M). The pH of the precipitation medium was maintained between 8 and 9 by addition of ammonia (28 wt%).

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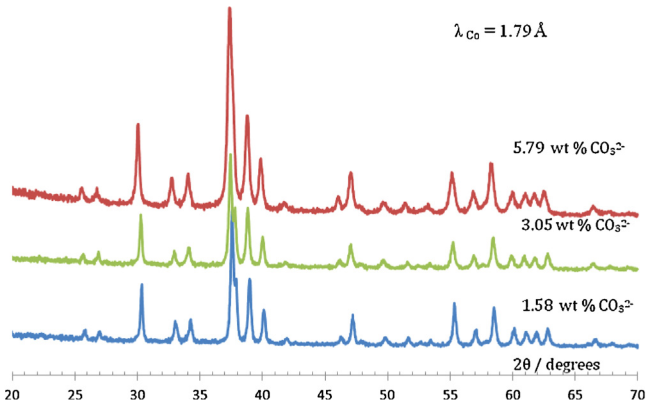

Fig. 1. Diffraction patterns of three B-CO_3-Fap samples.

The purity of the products was checked by infrared spectroscopy, X-ray diffraction and chemical analysis [10].

X-ray analysis was performed using an X-ray diffractometer MRD with a generator (40 kV and 40 mA). The scanning speed is 0.04° 2θ/s. X-ray diffractograms show thin rays indicating that all the solids are formed of a well crystallized phase whatever the amount of carbonate introduced.

Fig. 1 represents the X-ray diffractograms of three apatite samples. It shows characteristic peaks of apatite structure. The compounds crystallise in the hexagonal system, in the space group $P6_3/m$ [17]. The indexation of diffractogram in the hexagonal system was used to calculate the crystallographic parameters, with the “wincell” refinement program.

Table 1 gives the ‘a’ and ‘c’ parameters of various CO_3-Fap, preheated at 300 °C. For comparison, column 2 shows also the crystallographic parameters of the free carbonate phosphate fluorapatite together with the corresponding literature values. The parameter “a” decreases with increase in the rate of carbonate and the parameter “c” increases.

IR spectra were recorded using a Perkin–Elmer 7700 FT-IR spectrometer between 400 and 4000 cm^{-1} in KBr pellets. They present only bands characterizing apatite specimens, Fig. 2. Bands at 1037, 1110, and 964 cm^{-1} are attributed to the vibrational modes of $PO_4{}^{3-}$ groups [18,19]. Bands at 565 cm^{-1} and 706 cm^{-1} are assigned to P–O mode [20] and 469 cm^{-1} band results from the υ_2 phosphate mode [21]. In addition, the bands corresponding to $CO_3{}^{2-}$ ions in the B-CO_3-Fap appear at (876–1420–1463 cm^{-1}), and increase in intensity as $CO_3{}^{2-}$ amount increases [18,22]. The absence of bands between 600 and 1090 cm^{-1} shows that the products are free from $HPO_4{}^{2-}$ ions. However, parasite bands appear at 3450 cm^{-1}, 2890 cm^{-1} and 1400 cm^{-1}. They probably result from water retained by KBr.

The number of Ca^{2+}, $PO_4{}^{3-}$ and F^- ions in the unit cell of the apatite and the chemical formula of each synthesized sample are reported in Table 2.

Table 1
“a” and “c” parameters of the Ca-Fap and the B-CO_3-Fap.

$[CO_3^{2-}]/[PO_4^{3-}]$	0/CaFap	0.5	2	4
“a” parameter/Å	9.372(3) 9.371[a]	9.355(3)	9.333(9)	9.300(10)
“c” parameter/Å	6.884(2) 6.890[a]	6.900(2)	6.903(5)	6.914(6)

[a] Literature values [18].

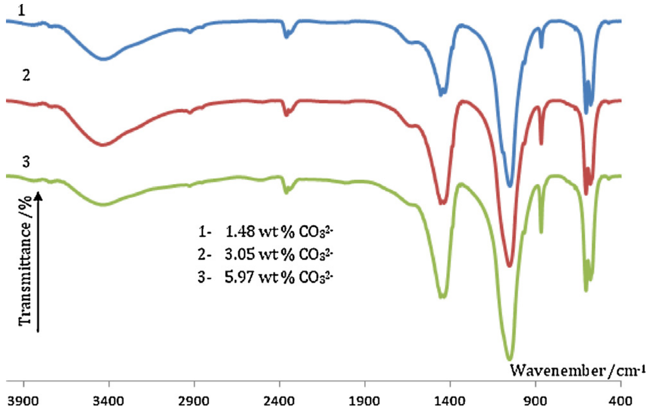

Fig. 2. Infrared spectra of three B-CO_3-Fap samples.

2.2. Calorimetric study

The attack reaction was followed using a C-80 SETARAM microcalorimeter using the reversal cells. Different masses of apatite were dissolved in 4.5 mL of the phosphoric acid solution (19% w/w P_2O_5) [10]. Various amounts of B-CO_3-Fap were placed in the lower compartment of the cell and a constant volume of phosphoric acid solution in the upper compartment which was tightly separated from the former by a metallic cover. The reactants were mixed using the reversing mechanism after a stabilization time of 12 h, which allows the calorimeter jacket to be alternatively in the reversal then the upward position. The device was checked by key dissolution reactions [23].

2.3. Thermochemical and kinetic studies

2.3.1. Thermochemical study

This study was performed at 25 °C with different masses of apatites and at different temperatures with a mass close to 25 mg for all the apatites.

2.3.1.1. At 25 °C. For each B-CO_3-Fap, the heat energy determined by integrating the rough signal is linear over the mass of the solid dissolved (10–60 mg) [10]. The slopes of the lines lead to the molar enthalpies of dissolution as reported in Table 3.

The molar enthalpy of dissolution of B-CO_3-Fap is around −200 kJ mol^{-1}. This quantity is lower than that determined for the free carbonate fluorapatite in the same solution (−171 kJ mol^{-1} [23]), therefore the introduction of carbonate in the apatite structure seems to decrease the molar enthalpy of the acid dissolution.

2.3.1.2. At different temperatures. The behavior of these phosphates toward the attack by phosphoric acid solution was performed in the 25–55 °C intervals by dissolving around 25 mg of solid in 4.5 mL having 19% weight P_2O_5 solution. Fig. 3 gives the variation of molar enthalpy ΔH_{mes} determined by integration of the row signal, as a function of temperature.

Increasing temperature in the 25–55 °C interval leads to a monotonic increase in the molar enthalpy of dissolution for all B-CO_3-Faps studied. This result is different from that found by Brahim et al. [7] for fluorapatite (Fap) who reported an extremum at about 45 °C attributed to a modification in the attack mechanism. Antar et al. [8] have also observed such phenomenon when dissolving Fap in a mixture of phosphoric and sulfuric acid solution.

2.3.2. Kinetic study

The kinetic study was performed on deconvoluted thermogramms in order to determine the kinetic parameters of