

# Cadmium fixation by synthetic hydroxyapatite in aqueous solution—Thermal behaviour

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## Abstract

This study deals with the mechanism of the cadmium uptake by synthetic hydroxyapatite (HA:  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) in aqueous solution. The rate of cadmium fixation by hydroxyapatite was investigated at 10 and 50 °C using batch experiments. Inductively coupled plasma atomic emission spectrometry, X-ray diffraction, FT-IR spectroscopy and electron microscopy were used to characterize the starting HA and the samples. The thermal behaviour of the powders was determined with the help of three thermoanalytical techniques (TGA, DTA, and MS) and temperature programmed X-ray diffraction. Cadmium immobilization kinetics can be divided into two steps: substitution of  $\text{Ca}^{2+}$  ions by  $\text{Cd}^{2+}$  in the HA lattice at the particle's surface, followed by their incorporation into the hydroxyapatite bulk. This results in the formation of an apatite solid solution, which is very important because in this way decontamination and storage can be performed with the same material.

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## 1. Introduction

Calcium phosphate apatites are the main inorganic constituents of biological hard tissues such as bones or teeth. The general formula of apatites is  $\text{Me}_{10}(\text{XO}_4)_6\text{Y}_2$ , where Me is a bivalent cation,  $\text{XO}_4$  a trivalent anion, and Y a monovalent anion. Apatites can accept numerous substitutions either on anionic or cationic sites. Nounah and Lacout [1] showed that a continuous series of solid solutions of cadmium and calcium hydroxyapatites can be prepared by an aqueous precipitation method. Cadmium is dangerous for human health and ecosystem. A chronic intoxication by cadmium can have serious consequences on the kidneys, the lungs and the bones (osteoporosis). The main sources of cadmium in natural waters are industrial wastes and phosphate fertilizers.

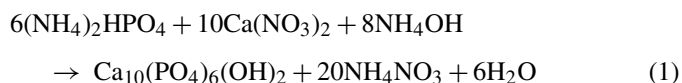
For more than 10 years, phosphates and more particularly apatites have been studied in decontamination methods for waste industrial aqueous solution and polluted water. Apatites are also studied as host matrices for the storage of separate radioactive

wastes. Previous studies showed that hydroxyapatites have a high removal capacity for  $\text{Cd}^{2+}$  and other toxic metal ions ( $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$ ) in aqueous solution [2]. Unfortunately, the fixation mechanism remains misunderstood. In the present work, we tried to characterize more accurately the interaction mechanism between the  $\text{Cd}^{2+}$  cations and the hydroxyapatite particles in aqueous solution. To this end, after the fixation experiments, the thermal behaviour of the loaded powders was investigated.

## 2. Experimental

### 2.1. HA powder

The hydroxyapatite (HA) powders were prepared by an aqueous precipitation method, according to the reaction:



A diammonium hydrogen phosphate aqueous solution ( $(\text{NH}_4)_2\text{HPO}_4$ ) was added to a calcium nitrate solution ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) using a peristaltic pump. The pH of the solution was regulated at a value of 9 by the addition of an ammonium hydroxide solution using a pH stat (Hanna Instruments). The

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temperature was controlled and maintained at 95 °C with automated apparatus. The suspension was continuously stirred and refluxed. After total addition of the  $((\text{NH}_4)_2\text{HPO}_4)$  aqueous solution, the suspension was matured during 30 min. Then, it was filtered and washed with 250 mL of distilled water. Finally, the precipitate was dried at 90 °C for at least 24 h.

The influence of the hydroxyapatite specific surface area (35.7, 22.1, 11.2 and 7.0  $\text{m}^2/\text{g}$ ) on the  $\text{Cd}^{2+}$  fixation was studied with samples having undergone different thermal treatments in air atmosphere (400, 700, 900 and 1000 °C during 1 h, respectively).

## 2.2. Characterization methods

The chemical compositions of the starting powder, of the exchanged one, and of the aqueous solutions were determined by inductively coupled plasma atomic emission spectrometry (ICP/AES), with a Thermo-Opteck Iris model.

The starting solids were controlled with phenolphthalein after a calcination at 1000 °C, according to a standard procedure [4]. This reagent allows to display the presence of calcium oxide.

Structural analyses were carried out by X-ray diffraction (XRD) of raw powders and powders calcined at 1000 °C for 15 h. Powder X-ray diffraction were recorded with Cu K $\alpha$  radiation on a  $\theta/2\theta$  diffractometer (Siemens, model D5000). The crystalline phases were determined from a comparison of the registered patterns with the ICDD powder diffraction files processed on EVA software (Bruker AXS). The diffraction patterns were recorded in the  $2\theta$  range 23–39° with a step of 0.03° and a count time of 5 s.

The surface area of powders was determined by the BET method 8 points (Analyser Micromeritics ASAP 2010) after degassing under vacuum at 150 °C. The granulometric distribution of the powder was measured using a CILAS 1064 laser granulometer (France).

The samples were also examined by scanning electron microscopy with a JEOL JSM-7400 F microscope. Fourier transformed IR absorption spectroscopy was used to study the powder characteristics that were not detectable by X-ray diffraction, such as carbonate or cadmium-containing hydroxyapatite. The spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrometer. They were recorded over the 4000–400  $\text{cm}^{-1}$  region with a resolution of 2  $\text{cm}^{-1}$ . All the spectra were normalized in respect to the  $\nu_4$  band (602  $\text{cm}^{-1}$ ).

## 2.3. Thermal analysis

Three thermoanalytical techniques were used to characterize the thermal behaviour of the powder samples: thermogravimetric analysis (TGA), differential thermal analysis (DTA) and mass spectrometry (MS). Thermogravimetric and differential thermal analysis were carried out simultaneously, in helium flow (80 mL/min), using a TA Instruments SDT 2960 apparatus. The heating rate was 10 °C/min and the powder mass was approximately 20 mg. The analysis of evolved gas was performed using a quadrupole mass spectrometer (Pfeiffer Vacuum Thermostar) coupled together with the previous apparatus.

Temperature programmed X-ray diffraction was used to determine the different crystalline phases formed during the heat treatment. The samples were heated in an Anton Parr HTK 16 high-temperature furnace, and XRD measurements were carried out in situ by a Bruker D8 Advance  $\theta/\theta$  diffractometer.

## 2.4. Cadmium fixation experiments

The amount of cadmium retained by the hydroxyapatite powder as a function of soaking time was determined by “batch experiments”. These experiments were undertaken in 100 mL closed Pyrex erlenmeyer under mechanical stirring (400 rpm). Each one was loaded with 0.700 g of HA. Cadmium aqueous solution was obtained by dissolving cadmium nitrate (Aldrich 99%) in distilled water.

The fixation experiments were composed of three steps. First, 50 mL of distilled water was introduced into the erlenmeyer containing the HA powder. This suspension was stirred for 24 h, at the work temperature, in order to reach a thermodynamical equilibrium between the solid and the liquid phases. Thus, the HA was at the “equilibrium of dissolution” (HAed). Then, an aliquot of 50 mL of 0.01394 M cadmium containing aqueous solution was added to each erlenmeyer. These conditions were chosen in order to have approximately 1 mol of cadmium per mol of HA (for 10  $\text{Ca}^{2+}$ ). Finally, for all the experiments the pH was not stabilized. After a soaking time “ $t_{\text{contact}}$ ”, the suspension was filtered and the powder was dried at 80 °C for 24 h. All the experiments were performed in duplicate.

## 3. Experimental results

### 3.1. Starting hydroxyapatite powder

Synthesis conditions (pH, temperature, Ca/P molar ratio of initial reagents) were adjusted in order to synthesize a stoichiometric hydroxyapatite, i.e., an HA having a Ca/P molar ratio equal to 1667 (10/6). If this condition is not verified, different phases form after thermal treatment at temperatures above 800 °C. The calcium deficient apatites ( $1.5 < \text{Ca/P} < 10/6$ ) are decomposed into  $\beta$ -tricalcium phosphate ( $\beta$ -TCP:  $\text{Ca}_3(\text{PO}_4)_2$ ) and stoichiometric hydroxyapatite (HA). For a ratio higher than 10/6 a mixture of apatite and calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) is precipitated that changes into stoichiometric hydroxyapatite and lime (CaO) during heating [3].

The starting CaHA powder with a surface area of  $35.7 \pm 0.5 \text{ m}^2 \text{ g}^{-1}$  has a broad granulometric distribution with diameters ranging from 0.4 to 36  $\mu\text{m}$  (not presented). The average grain size calculated from the formula  $\emptyset = 6/(\rho S_{\text{BET}})$ , gives an equivalent diameter close to 53 nm.

The X-ray diffraction patterns of the starting HA powder (after heating at 400 °C) is given in Fig. 1a. The profile is characteristic of a single phase apatite. The FT-IR spectrum of this powder (Fig. 1b) shows mainly the HA bands but weak bands at 1540, 1450, 1416 and 880  $\text{cm}^{-1}$  are observed. These can be unambiguously assigned to the vibration bands  $\nu_2$  and  $\nu_3$  of the  $\text{CO}_3^{2-}$  groups [5].

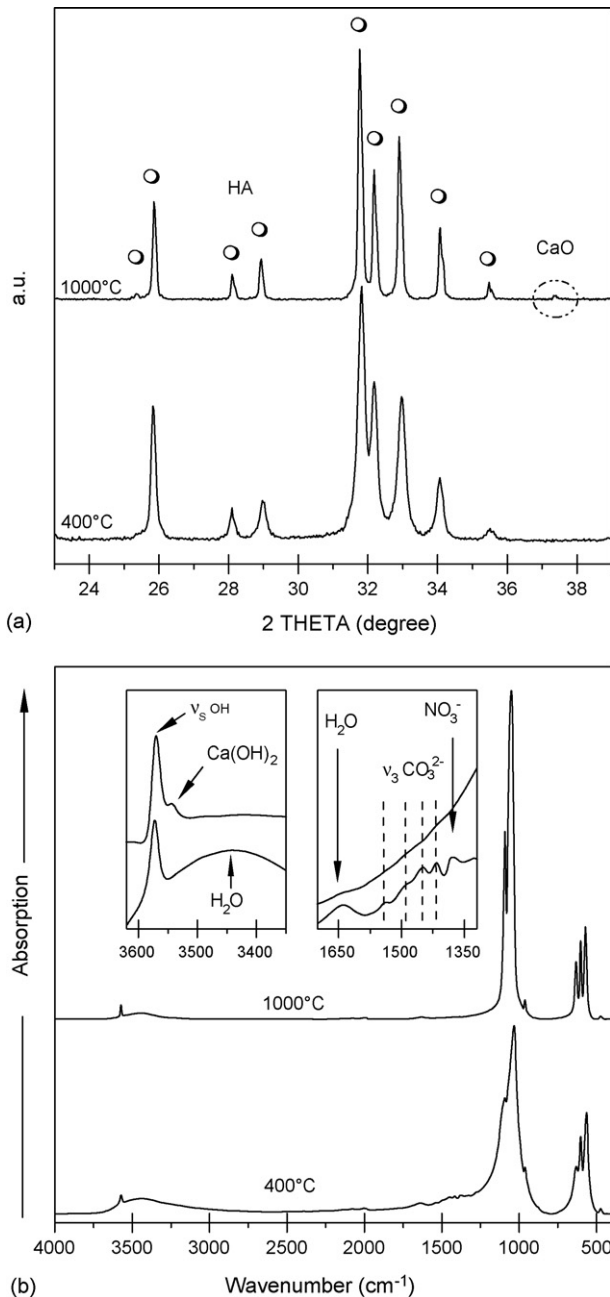


Fig. 1. (a) X-ray diffraction patterns and (b) FT-IR spectra of starting HA after heat-treatment at 400 °C during 1 h, and 1000 °C during 15 h.

After calcination in air between 800 and 900 °C, the FT-IR spectra of the starting HA show Ca(OH)<sub>2</sub> bands at 3641 and 3544 cm<sup>-1</sup> (Fig. 1b). This compound corresponds with the CaO traces detected on the XRD diagram registered immediately after calcination at 1000 °C for 15 h (Fig. 1a), and by a positive phenolphthalein test. This formation of lime relates to the disappearance of the bands attributed to the stretching vibration of carbonates. Accordingly, the weight loss of the starting HA between room temperature and 900 °C determined by TGA is slightly more important than for a pure HA; 3.20 and 2.60%, respectively.

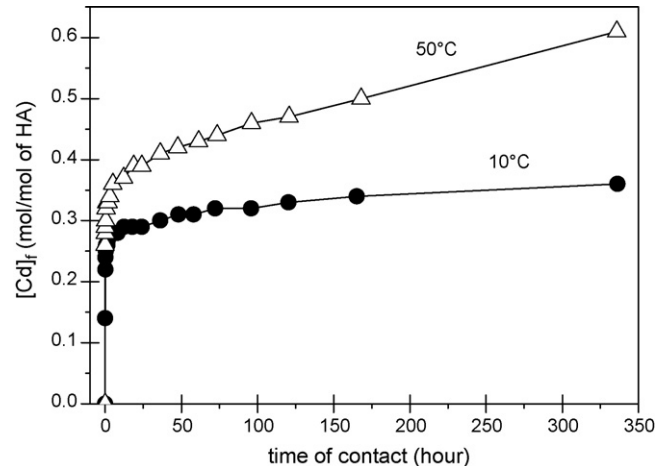


Fig. 2. Amount of Cd<sup>2+</sup> fixed per mol of HA (36 m<sup>2</sup>/g), for  $n_{\text{Cd}}/n_{\text{starting HA}} = 1$  and  $T = (\bullet)$  10 or  $(\Delta)$  50 °C, vs. the soaking time.

These results indicate that the starting HA is composed of a lightly carbonated HA that decomposes into stoichiometric HA and CaO during heating. The ratio of this second phase, determined by XRD [6], is only 0.3 wt%. The corresponding Ca/P molar ratio of the starting HA is equal to  $1.677 \pm 0.008$ .

As the experiments are realized in aqueous solution, the reference apatite is not the starting HA but the powder spring from the suspension at the dissolution equilibrium (HAed). The XRD, FT-IR, and thermoanalytical results of HAed are exactly the same as the starting HA whatever the bath temperature might be. So, all the conclusions given for the starting HA are valid for the HAed. This confirms that the starting HA has not undergone any modification when the suspension turns equilibrium.

### 3.2. Fixation of cadmium

The level of cadmium fixation, at two temperatures (10 and 50 °C), is reported in Fig. 2.

The amount of cadmium fixed by the HA powder [Cd]<sub>f</sub> increases with the time of contact ( $t_{\text{contact}}$ ) and the bath temperature ( $T_{\text{bath}}$ ). At 10 °C, the amount of cadmium tends toward a quasi constant value of about 0.34 mol per mol of HA after 120 h. At 50 °C, no threshold is reached. In agreement with Fedoroff et al. [7], the value reached at 10 °C is not an equilibrium value but should continue to increase slowly. The cadmium fixation can be decomposed into two steps. During the first 10 min, the fixation is characterized by a high rate, whatever the bath temperature may be. Then the rate decreases notably for longer times.

### 3.3. Characterization of the loaded powders

The diffraction patterns of the uncalcined soaked samples (not presented) are typical for hydroxyapatite. No other crystalline phase is detected whatever the parameters ( $t_{\text{contact}}$  and  $T_{\text{bath}}$ ).

Some changes are noticed on the FT-IR spectra (Fig. 3). Neither the position, nor the relative intensity of the bands  $\nu_L$ ,  $\nu_4$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_5$  of the HA have changed. But, the band  $\nu_1$

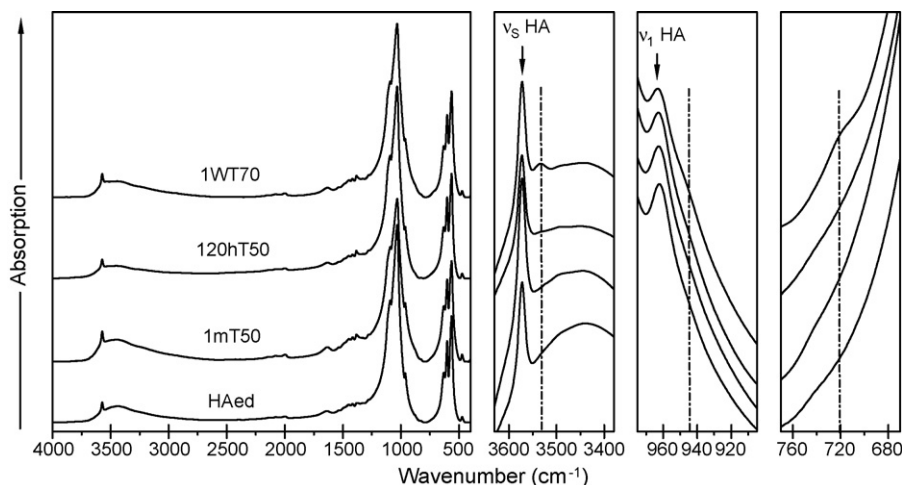


Fig. 3. FT-IR spectra of HAed, and uncalcined samples 1mT50, 120hT50 and 1WT70. The samples were soaked during 1 min at 50 °C, 120 h at 50 °C, and 1 week at 70 °C, in a cadmium aqueous solution ( $n_{\text{Cd}}/n_{\text{HA}} = 1$ ), respectively.

becomes broader, less intense and its maximum moves to a higher wavenumber when  $[\text{Cd}]_f$  increases. Additionally, a broad shoulder between 950 and 945  $\text{cm}^{-1}$  appears whose relative intensity increases with  $[\text{Cd}]_f$ . A second shoulder at 3534  $\text{cm}^{-1}$  grows similarly. The latter becomes a well defined peak for the samples 1WT70 and 2WT70. These samples, obtained at 70 °C after respectively 1 and 2 weeks of experiment, exhibit also an IR shoulder at 720  $\text{cm}^{-1}$ . The vibrational bands of residual nitrates and carbonates are also visible with the same relative intensity as the starting HA.

Fig. 4 shows the SEM micrographs of the starting HA and sample 78hT30 obtained after 78 h in cadmium aqueous solution ( $6.97 \times 10^{-3} \text{ M}$ ) at 30 °C. The starting HA powder is formed of rod-shaped agglomerated crystallites (Fig. 4a). After soaking in aqueous solution under stirring conditions, the crystallites are slightly more rounded than the starting HA, as shown in the example of sample 78hT30 (Fig. 4b). No other solid and a uniform distribution of cadmium at the particles surface are shown by energy dispersive X-ray spectrometry (EDX).

### 3.4. Thermal behaviour of samples

Thermal analyses were carried out on the samples 3mT10, 1WT10, 1mT50 and 120hT50 that were obtained after 3 min and 1 week in cadmium aqueous solution ( $6.97 \times 10^{-3} \text{ M}$ ) at 10 °C, and 1 min and 120 h in the same solution at 50 °C, respectively.

Between the room temperature and 700 °C, no new phase is detected by X-ray diffraction. Conversely, between the ambient temperature and 400 °C, a new shoulder appears at 747  $\text{cm}^{-1}$  on the FT-IR spectra. Furthermore, as for HAed, the nitrate and carbonate bands disappear between 600 and 800 °C, and 600 and 900 °C, respectively.

Above 700 °C, two new phases are detected by X-ray diffraction. The first one identified as cadmium oxide, forms between 700 and 800 °C. The second one appears between 950 and 975 °C. The observed lines could be indexed according to the monoclinic phase  $\text{Ca}_3(\text{PO}_4)_2$   $\alpha$ -TCP. The more  $[\text{Cd}]_f$  increases,

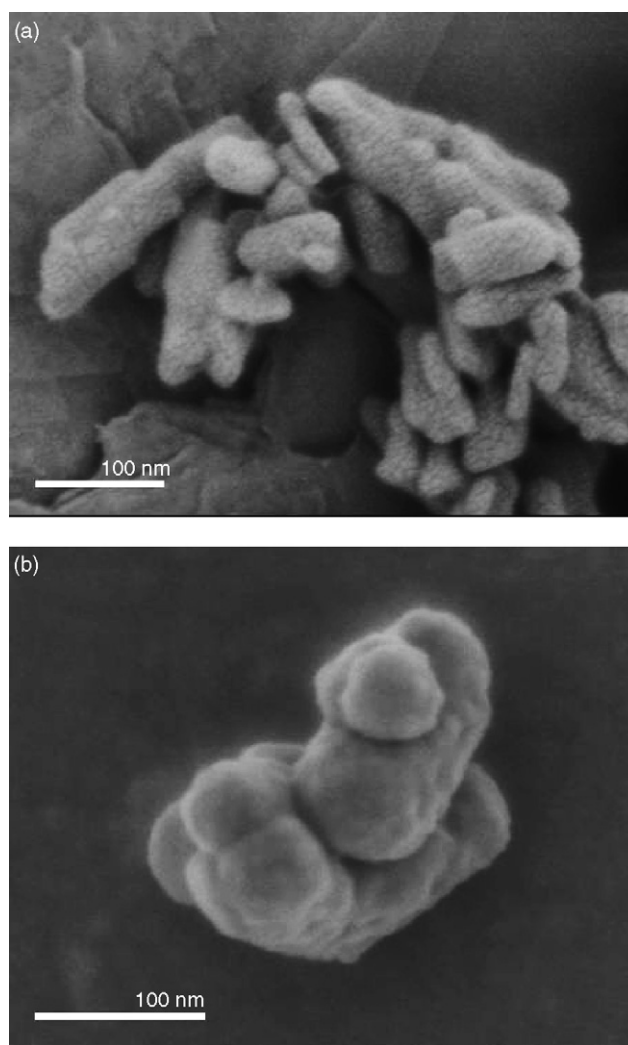


Fig. 4. SEM micrographs of (a) the starting HA and (b) the sample 78hT30.

the more the ratio of intensities  $I_{\alpha\text{-TCP}(034)}/I_{\text{HA}(211)}$  increases. Moreover, between 900 and 1000 °C, compared with HAed, the IR shoulder at 747  $\text{cm}^{-1}$  disappears, and three new shoulders appear at 990, 675 and 550  $\text{cm}^{-1}$ .



Table 1  
Thermogravimetric analysis results for HAed and some samples after fixation experiments

	Weight losses $\Delta P$ (%)				Total	[Cd] <sub>f</sub> (mol/mol HA)
	50–600 °C Zone I	600–800 °C Zone II	800–1300 °C Zone III	1300–1375 °C Zone IV		
HAed	1.87	1.00	1.78	0.34	4.99	0.00
3mT10	2.02	1.23	4.57	0.38	8.20	0.20
1WT10	1.96	1.30	5.86	0.27	9.39	0.33
1mT50	2.11	1.27	5.26	0.28	8.92	0.25
120hT50	1.94	1.28	7.82	0.16	11.20	0.47

Also, the thermal treatment induces a change of colour. At room temperature the powders are white. Then, they turn gradually from orange to brown between 700 and 1000 °C. Above 1000 °C, the powders become white again.

The TGA results allowed to distinguish four successive weight losses that are summarized in Table 1.

The first one (I), due to the released of adsorbed water in the temperature range 50–600 °C, is almost the same for all samples.

The second one (II), between 600 and 800 °C, corresponds to the release of synthesis residues. The weight loss is slightly more important after cadmium fixation but quite independent of the amount of immobilized cadmium. A slight water emission (*m/z* 18) is also recorded by MS between 700 and 800 °C.

In the third domain (III), between 800 and 1300 °C, the weight loss recorded for samples soaked in Cd containing solution differs from that of HAed powder. The weight loss rate (DTG) shows two successive peaks (Fig. 5a). Each one is accompanied with an endothermic reaction observed by DTA (Fig. 5b). The maximum rates occur between 900 and 950 °C for the first weight loss (noted ①), and from 1000 up to 1050 °C for the second one (noted ②). The latter increases strongly with [Cd]<sub>f</sub>, whereas the first one changes little whatever the sample composition may be. The same variation is noted for their endothermic event. MS results show water evolution between 950 and 1050 °C. The relative intensity of this H<sub>2</sub>O peak increases with [Cd]<sub>f</sub>. This peak is absent for the starting HA and HAed. Moreover, between 850 and 1300 °C, a continuous weight loss is observed as for HAed. It is associated with the HA dehydroxylation. The slope of this weight loss decreases with [Cd]<sub>f</sub>. At the same time, the relative intensity of the broad HA dehydroxylation endothermic event decreases as [Cd]<sub>f</sub> increases (Fig. 5b).

The fourth domain of weight loss (IV) occurs in the temperature range 1300–1350 °C, and is similar for all the compounds. It is due to the HA decomposition into tetracalcium phosphate, tricalcium phosphate and water. The more the quantity of immobilized cadmium increases, the more this weight loss decreases till it disappears for [Cd]<sub>f</sub> greater than about 0.70 mol per mol of starting HA.

#### 4. Discussion

The amount of immobilized cadmium (in mol of Cd per mol of starting HA), after 2 h at 30 °C, is reported versus the HA

surface area in Fig. 6a. A linear plot is obtained, and this amount is constant when it is normalized with respect to the surface area. More, whatever the bath temperature or the time of contact may be, the quantity of fixed cadmium remains always equal to the quantity of released calcium (Fig. 6b).

These results highlight that cadmium fixation is mainly controlled by the powder surface. But these observations are compatible with two mechanisms: an ion exchange, or a heterogeneous dissolution precipitation.

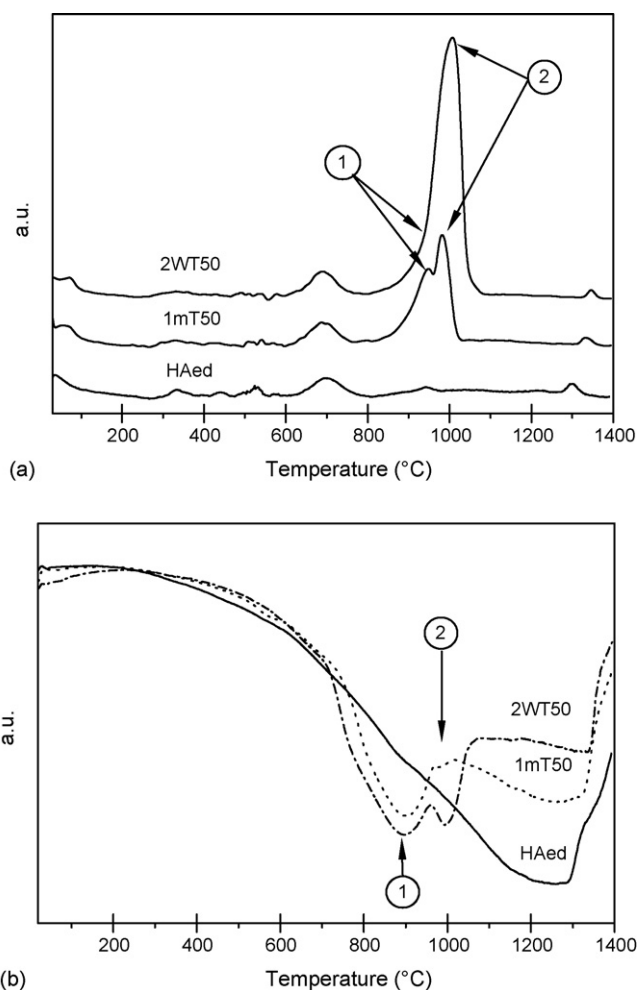


Fig. 5. (a) Derivative plots of TGA curves (DTG), and (b) DTA results for HAed and samples 1mT50 and 2WT50 obtained after 1 min and 2 weeks of experiment, for  $n_{\text{Cd}}/n_{\text{HA}} = 1$  and  $T = 50$  °C, respectively.

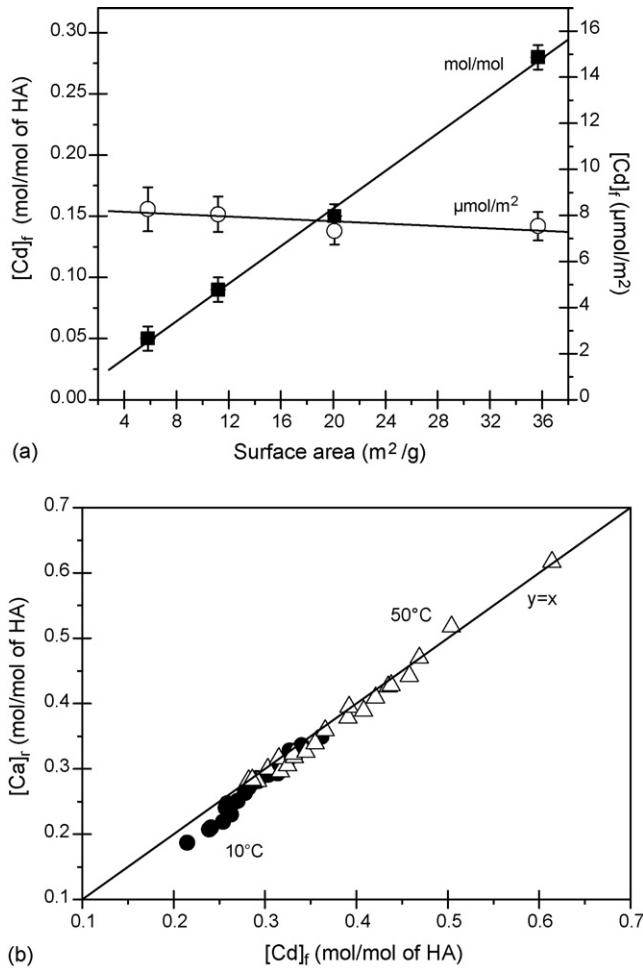
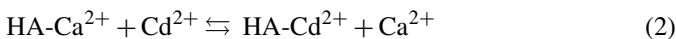
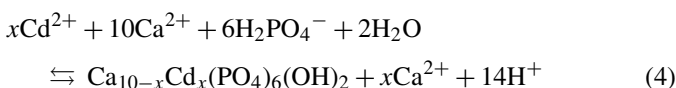
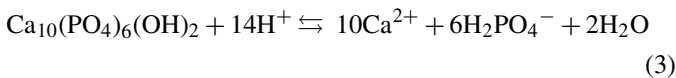


Fig. 6. (a) Amount of  $\text{Cd}^{2+}$  fixed as function of the surface area; for  $n_{\text{Cd}}/n_{\text{HA}} = 1$ ,  $T = 30^\circ\text{C}$ , and 2 h experiment. (b) Amount of  $\text{Ca}^{2+}$  released into the solution as a function of the amount of  $\text{Cd}^{2+}$  fixed by the HA; for  $n_{\text{Cd}}/n_{\text{HA}} = 1$ ,  $T = (\bullet) 10$  and  $(\Delta) 50^\circ\text{C}$ , and 2 weeks  $\geq t_{\text{contact}} \geq 1$  min.

The cadmium and calcium exchange is described by the following general reaction:



The speciation calculation of triacid  $\text{H}_3\text{PO}_4$  reveals that  $\text{H}_2\text{PO}_4^-$  dominates the aqueous phosphate concentration in the lower pH range of this study ( $\text{pH}_{\text{zpc}} > 6 \geq \text{pH} \geq 4$ ). Thus, dissolution and precipitation can be depicted respectively by:



The cadmium uptake mechanism by the HA could be divided into two processes:

- First, the  $\text{Cd}^{2+}$  could be adsorbed at the HA surface on specific sites.

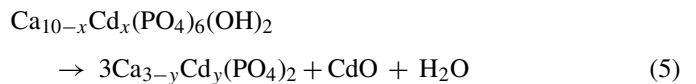
- Then, either  $\text{Cd}^{2+}$  could diffuse into the apatitic structure, or a dissolution precipitation process could occur from the cadmium adsorbed.

The end product of these reactions would be a cadmium-containing hydroxyapatite, or an amorphous mixed phosphate.

After the fixation experiments, and before heating, no argument allows to conclude that a solid solution is formed. However, the FT-IR spectra show new bands or shoulders, at  $3534\text{ cm}^{-1}$  ( $\nu_{\text{S}}$ ),  $747\text{ cm}^{-1}$  ( $\nu_{\text{L}}$ ) or  $950\text{ cm}^{-1}$  ( $\nu_{\text{1}}$ ), which have been attributed by Nounah and Lacout [1] to cadmium-containing hydroxyapatite.

The thermal treatments reveal the formation of cadmium oxide above  $700^\circ\text{C}$ . The powders seem coated with a coloured cadmium oxide (orange–brown). The  $\text{CdO}$  formation comes from the decomposition of the hydrated  $\text{Cd}^{2+}$  cation at the surface of the powder. The water evolved recorded by MS confirms this assumption.

From  $950$  to  $975^\circ\text{C}$ ,  $\alpha$ -TCP and water are detected. According to Nounah and Lacout [1] and Romdhane et al. [8], these phases are due to the thermal decomposition of the cadmium-containing hydroxyapatite:



with  $x = 1 + 3y$  and  $0.55 < y < 1.00$  (i.e.  $4.00 \geq x \geq 2.65$ ).

This solid solution contains an amount of Cd ( $4.00 \geq x \geq 2.65$ ) greater than the amount of Cd introduced into the starting suspension ( $x \approx 1$ ). According to Nounah and Lacout [1], a solid solution with  $0 < x < 1$  decomposes into cadmium oxide,  $\beta$ -tricalcium phosphate, and lime from  $960^\circ\text{C}$ . These two last phases are absent from DRX diagrams, and the thermal analyses show that pure HA is still present above this temperature. This means that the exchanged powder is not a homogeneous solid solution, but composed of pure HA and cadmium-containing hydroxyapatite with  $4.00 \geq x \geq 2.65$ . The latter can be formed, either by intracrystalline diffusion of Cd into the superficial layer of the HA crystallites, or by precipitation from nucleation sites of the crystallites surface. In both cases, the crystallites are composed of a core of a pure HA surrounded with the solid solution.

According to the literature data [9], cadmium oxide sublimates from  $880^\circ\text{C}$ . This characteristic was used to separate the weight losses ① and ② described previously with the aim of determining the cadmium distribution during the fixation according to the experiment parameters. During this thermal treatment the cadmium oxide located at the surface of the HA will sublimate, whereas the Cd incorporated into the solid solution will remain in the HA. Four samples were used (referred in Table 2). Fig. 7a shows that after a prolonged heating of 30 h in air at  $895^\circ\text{C}$  all the cadmium oxide, formed between  $700$  and  $800^\circ\text{C}$ , is removed and the powder becomes white again. Moreover, the weight loss ① does not appear any more on the DTG plots (Fig. 7b). The shoulder at  $747\text{ cm}^{-1}$  ( $\nu_{\text{L}}$ ) disappears above  $950^\circ\text{C}$ , and the XRD patterns show  $\alpha$ -TCP and  $\text{CdO}$  again (Fig. 7a). The same decomposition is observed for a very fast heating rate ( $120^\circ\text{C}/\text{min}$ ) excluding any solid diffusion. These results and

Table 2  
Amount of cadmium in the powder before and after prolonged heating for 30 h at 895 °C

Sample	Experimental parameters		[Cd] <sub>f</sub> (mg of Cd/g of weighed powder)		Cd removed after 30 h at 895 °C	
	T <sub>bath</sub> (°C)	t <sub>contact</sub>	Before heating	After 895 °C–30 h	Powder (mg Cd/g)	(μmol/m <sup>2</sup> )
1mT10	10	1 min	13.6	3.3	10.3	2.6
2WT10	10	2 weeks	37.4	24.3	13.1	3.3
1mT50	50	1 min	27.4	15.4	12.0	3.0
120hT50	50	120 h	51.3	36.7	14.6	3.7

the presence of characteristic IR bands of cadmium-containing hydroxyapatite before heating confirm that the solid solution does not form during the thermal treatment but during the fixation experiments.

Table 2 gives the amount of cadmium in the powder before and after prolonged heating at 895 °C, as well as the amount of cadmium removed after this thermal treatment. The quantity of cadmium uptake in the solid solution ranges from 3 to 37 mg/g

of weighed powder according to the experimental parameters (*t*<sub>contact</sub> and *T*<sub>bath</sub>). The more these parameters increase, the more the quantity of cadmium in solid solution is important. Conversely, the quantities of Cd supposed to be at the HA surface change very little (10–15 mg/g). Furthermore, these values normalized with respect to the surface area of the powders are close to the number of sites ≡P–OH (4.1 μmol/m<sup>2</sup>) or ≡Ca–OH (4.8 μmol/m<sup>2</sup>) available on the surface of a grain.

These findings confirm that the first step of cadmium immobilization is the adsorption on individual sites of the hydroxyapatite surface. The second step is either a diffusion process of the adsorbed Cd<sup>2+</sup> in the apatitic structure, within a very low depth, or a cadmium-containing hydroxyapatite precipitation from adsorbed Cd<sup>2+</sup>. The unchanged morphology of the solid particles would privilege the first process, while the very low value of the diffusion coefficient in the HA (10<sup>–50</sup> to 10<sup>–70</sup> cm<sup>2</sup>/s) [10] would rather account for the second one. The solubility product (*K*<sub>SP</sub>) of CdHA and HA, determined by Mahapatra et al. [11], are very similar (9.6 × 10<sup>–153</sup> and 2.7 × 10<sup>–152</sup>, respectively) and do not allow any conclusion about this second step.

## 5. Conclusion

This study confirms that hydroxyapatites are efficient to immobilize cadmium in polluted aqueous solutions.

Cd<sup>2+</sup> cations substitute for the easiest accessible calcium at the HA surface. Then, these cadmium cations are incorporated into a solid solution Ca<sub>10–x</sub>Cd<sub>x</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> with 4.00 ≥ *x* ≥ 2.65. This one is formed either by a surface heterogeneous precipitation process, or by intracrystalline diffusion on a very low depth. Indeed, if it takes place, this diffusion occurs in the superficial layer of the crystallites and not into the bulk because the solid solution composition is in the range 4.00 ≥ *x* ≥ 2.65, while the quantity of cadmium introduced into the starting solution is 1 mol per mol of starting HA (*x* = 1). Whatever the mechanism involved the exchanged powder is composed of a core of pure HA, and a surrounding shell highly concentrated in cadmium.

The fact that cadmium is incorporated into a solid solution thermally stable up to 950 °C is very important for its stabilization. This enables to perform in situ immobilization of cadmium, followed by its storage in a single process. From this point of view, it appears interesting to further study the sintering of cadmium-containing hydroxyapatite below the decomposition temperature of the solid solution, this work is under progress.

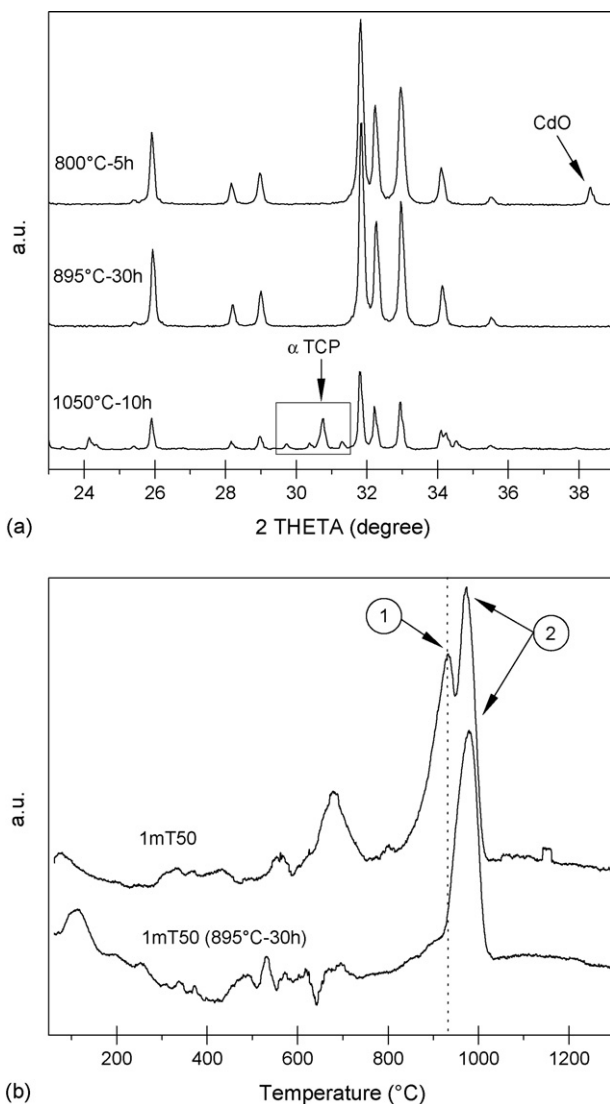


Fig. 7. (a) DRX patterns of the sample 120hT50 after various thermal treatments, and (b) derivative plot (DTG) of TGA of the sample 1mT50 before and after heating (30 h at 895 °C).

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## References

- [1] A. Nounah, J.L. Lacout, Thermal behavior of cadmium-containing apatites, *J. Solid State Chem.* 107 (1993) 444–451.
- [2] Q.Y. Ma, Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite, *Environ. Sci. Technol.* 28 (1994) 1219–1228.
- [3] S. Raynaud, E. Champion, D. Bernache-Assollant, P. Thomas, Calcium phosphate apatites with variable Ca/P atomic ratio. I. Synthesis, characterisation and thermal stability of powders, *Biomaterials* 23 (2002) 1065–1072.
- [4] AFNOR, Détermination quantitative du rapport Ca/P de phosphates de calcium, NF S 94-066, 1998.
- [5] J.-P. Lafon, Ph.D. Thesis, University of Limoges, 2004.
- [6] S. Raynaud, E. Champion, D. Bernache-Assollant, J.P. Laval, Determination of calcium/phosphorus atomic ratio of calcium phosphate apatites using X-ray diffractometry, *J. Am. Ceram. Soc.* 84 (2001) 359–366.
- [7] M. Fedoroff, J. Jeanjean, J.C. Rouchaud, L. Mazerolles, P. Trocellier, P. Maireles-Torres, D.J. Jones, Sorption kinetics and diffusion of cadmium in calcium hydroxyapatites, *Solid State Sci.* 1 (1999) 71–84.
- [8] S.S. Romdhane, G. Bonel, D. Louër, Etude chimique et structurale du système phosphate tricalcique-phosphate tricadmique, *Bull. Mineral.* 105 (1982) 343–346.
- [9] P. Baud, in: M. et Cie (Ed.), *Nouveau Traité de Chimie Minérale*, Paul Pascal, Paris, 1962, pp. 330–430.
- [10] D.J. Cherniak, W.A. Lanford, F.J. Ryerson, Lead diffusion in apatite and zircon using ion implantation and Rutherford Backscattering techniques, *Geochim. Cosmochim. Acta* 55 (1991) 1663–1673.
- [11] P.P. Mahapatra, H. Mishra, N.S. Chickerur, Solubility and thermodynamic data of cadmium hydroxyapatite in aqueous media, *Thermochim. Acta* 54 (1982) 1–8.