



CHAPTER 2

FABRICATION AND CHARACTERIZATION OF HYDROXYAPATITE CERAMICS

2.1 Introduction

Various methods have been proposed for the synthetic preparations of HAp powders in pure and homogeneous form. HAp powders may be synthesized from aqueous or nonaqueous systems. In the precipitation reaction, solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ are brought to pH 11 to 12 with concentrated NH_4OH . The phosphate solution is dropwise added to the stirred Ca solution (10-13).

Another method is the addition of H_3PO_4 to $\text{Ca}(\text{OH})_2$; the pH changes from 12.4 to 8.7 as the precipitation reaction proceeds (14). Hydrolysis of CaHPO_4 is carried out in a NaOH solution of low concentration for several hours at 25°C to 100°C or for 20 h in boiling distilled water (15). Hydrolysis of $\text{Ca}_3(\text{PO}_4)_2$ at temperatures in the range of 40 to 80°C at pH 3 to 7.5 results in the formation of a calcium-deficient hydroxyapatite (16). As a result of these different production ways, variation in compositional and structural properties are obvious. Important parameters are

1. The flow rate of the reagents, which controls the crystal size of the apatites.
2. The pH value at which the precipitation is carried out.
3. The presence of impurities which can easily be incorporated in the structure.

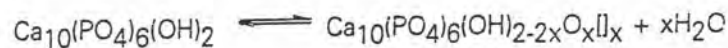
Apatites from nonaqueous systems can be prepared by solid state reactions at temperature above 900°C (17-19).

The crystal structure of HAp, has long been reported to occur as hexagonal crystals, but is now known that HAp tends to occur in a closely-similar pseudo-hexagonal monoclinic form (20). At high temperatures, the HAp structure may be modified depending upon its stoichiometry*, the temperature, the atmosphere, and the synthesis

* HAp ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is stoichiometric if the ratio of Ca to P is exactly 5:3 (1.67)

conditions. Most HAp synthesized from nonaqueous systems, such as by solid state reaction or by precipitation from a melt have the ideal HAp crystal structure without lattice contraction. In contrast, presence of HPO_4 and/or lattice H_2O is possible in aqueous apatites. This results in a contraction of the a-axis during heating at 200 and 400°C and in the formation of a mixture of HAp and tricalcium phosphate after pyrolysis at 850°C.

At higher temperature, the HAp can be totally or partially dehydrated. Above 850°C a small weight loss is recorded; during cooling an equivalent increase in weight is observed. Those observations indicate a slight reversible dehydration of the HAp according to reaction

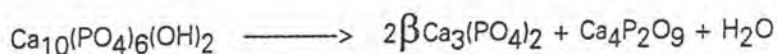


[] denotes a vacancy in the OH^- sublattice.

This reaction is an equilibrium reaction and the reaction product may be influenced by the partial H_2O pressure. If H_2O is added, the reaction shifts to the left, thus stabilizing the HAp. The structure of the HAp is then preserved up to 1100 °C. Pyrolysis (decomposition as a result of heat) in vacuum or in gasses free of water shifts the reaction to the right and an oxyhydroxyapatite is formed, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{O}_x[\text{}]_x$.

In the limit, when $x=1$, oxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6\text{O}$, is formed (21). This reaction product exists only in the temperature range of 850 to 1050°C. It is highly reactive and at temperatures lower than 800°C, it undergoes a small rehydration giving rise to oxyhydroxyapatite. This is stable in air at room temperatures (22-23).

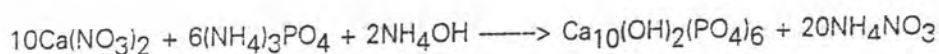
From 1050°C on, the hydroxyapatite may be decomposed according to reaction



At temperatures higher than 1350°C $\beta\text{Ca}_3(\text{PO}_4)_2$ transforms to $\alpha\text{Ca}_3(\text{PO}_4)_2$ (2). The α phase, a polymorphic form of β , is the high-temperature phase which is maintained upon cooling.

2.2 Preparation of HAp powders

In this work HAp powders were prepared using a method based upon the precipitation technique reported by Jarcho et al (12), which involves the use of $(\text{NH}_4)_2\text{HPO}_4$ and $\text{Ca}(\text{NO}_3)_2$ solutions. Precipitation reaction between a solution of calcium nitrate-4-hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and a solution of diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) in base medium occurs according to the reaction (10).



2.2.1 Construction of Some Processing Facilities

The following processing facilities were designed and constructed:

- (i) Adjustable Speed Stirrer with Teflon Paddle (Fig. 2.1)
- (ii) Suction filtered system (Fig. 2.3)

2.2.2 Exploratory Tests

Fig.2.5 is a flow chart for the precipitation method used to synthesize the HAp powder.

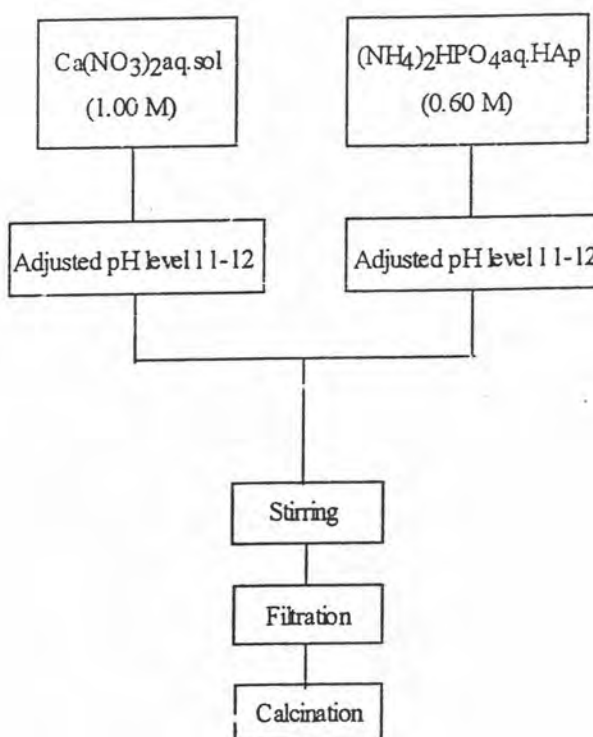


Fig.2.5 Flow chart showing HAp synthesis through precipitation method.



Fig.2.1 Photograph of adjustable speed stirrer with teflon paddle.

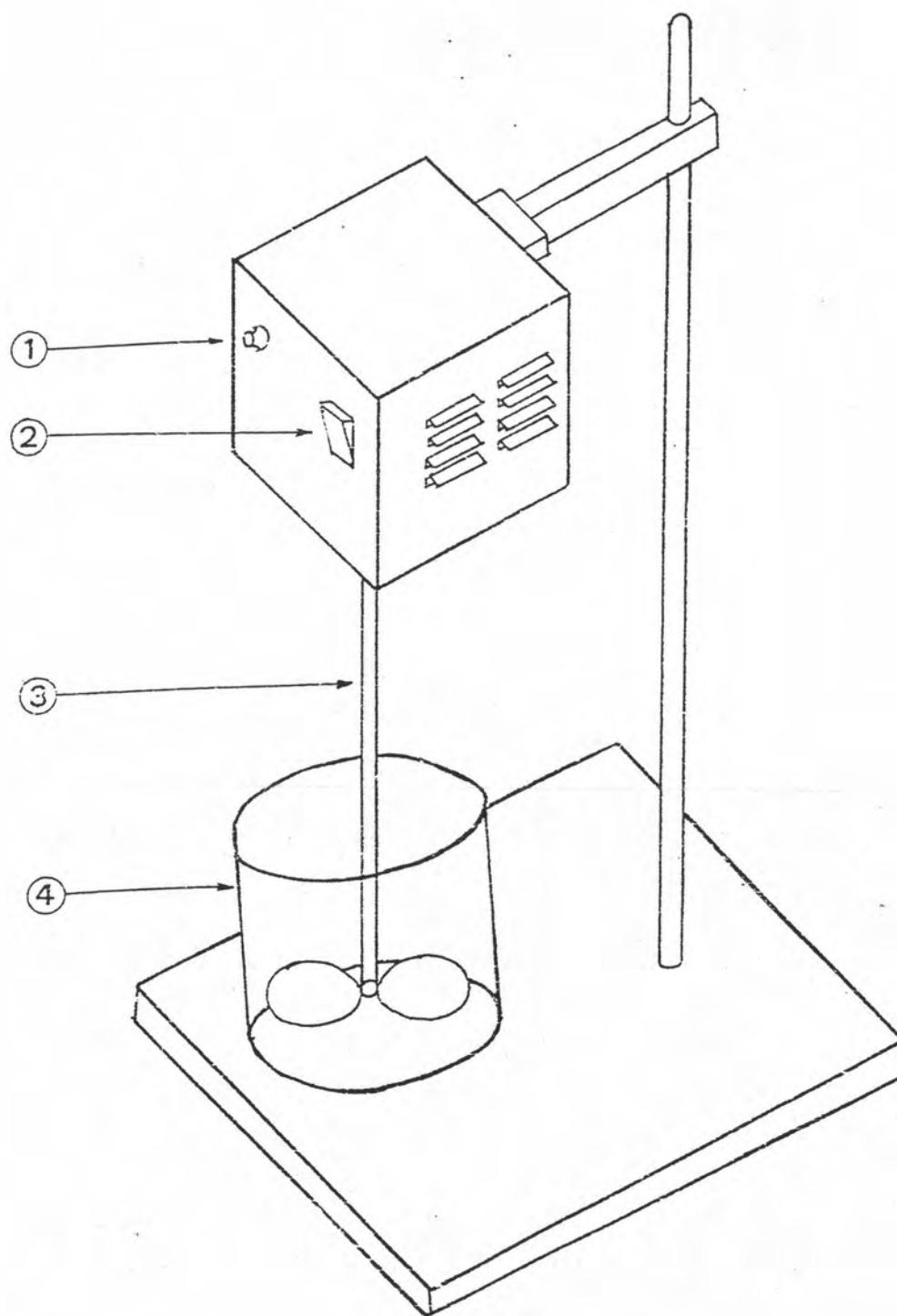


Fig.2.2 Schematic arrangement of stirring system assembly :

(1) speed adjust knob, (2) power switch, (3) tefion paddle, (4) container

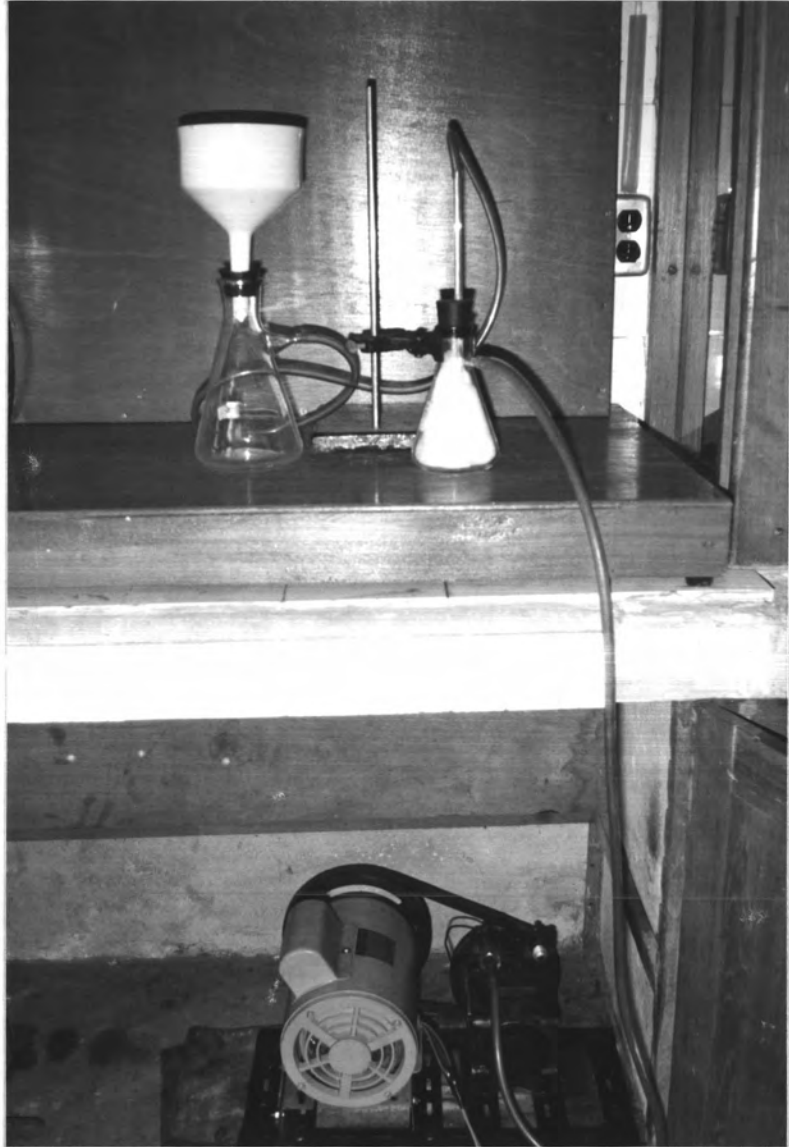


Fig.2.3 Photograph of suction filtered system.

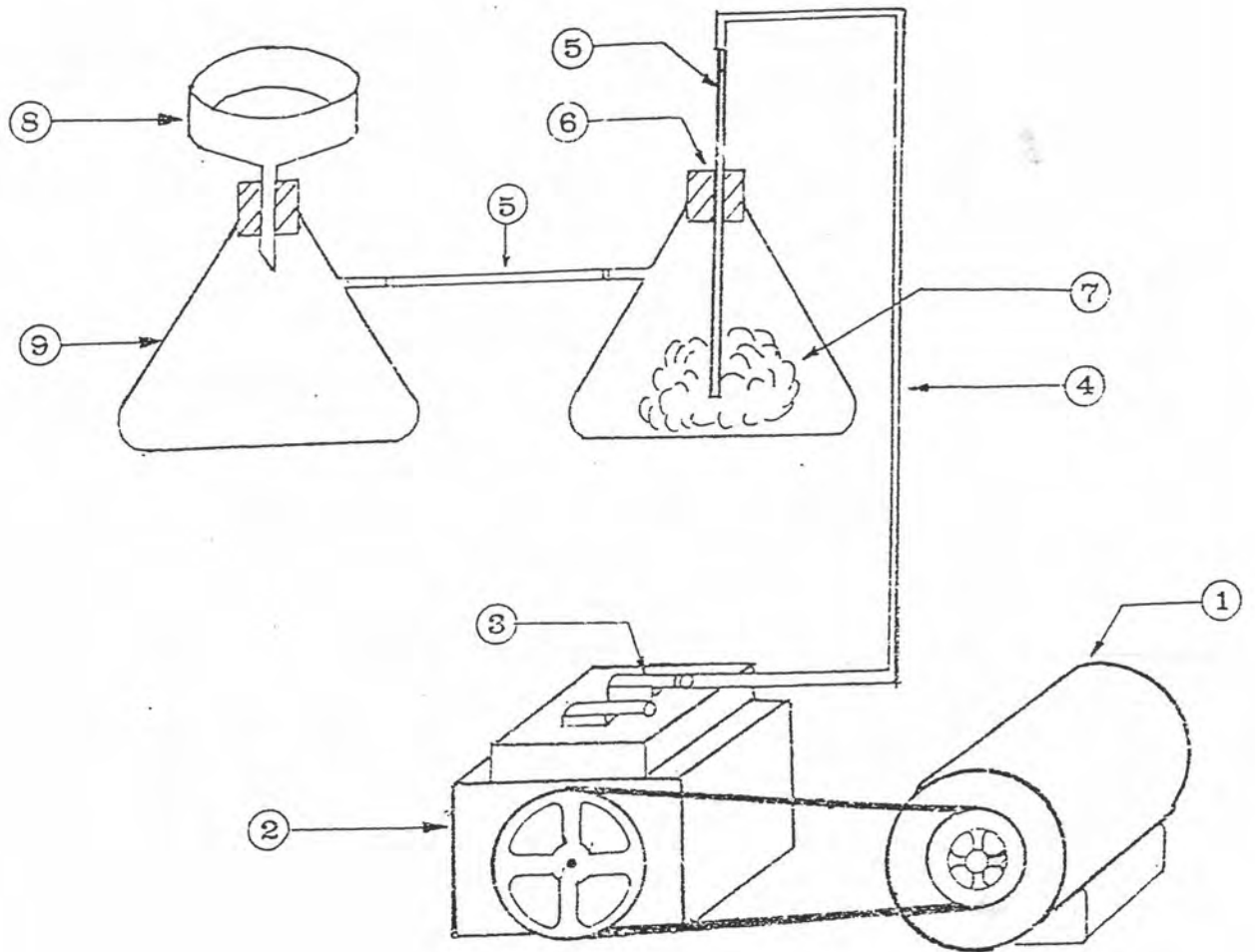


Fig.2.4 Schematic arrangement of suction filtered system :

- (1) motor, (2) rotary compressor, (3) suction pipe, (4) rubber tube,
 (5) glass tube, (6) rubber cork, (7) cotton, (8) buchner funnel.

A solution of $\text{Ca}(\text{NO}_3)_2$ of 1.00 M concentration and a solution of $(\text{NH}_4)_2\text{HPO}_4$ of 0.60 M concentration were brought to pH 11 to 12 with concentrated NH_4OH . The phosphate solution is dropwise added to the stirred calcium solution. The reaction mixture was left overnight to allow the precipitation to settle. The precipitate was filtered and calcined.

To enable us to successfully prepare our own HAp powder by the precipitation technique as outlined above, the effect of various parameters on the crystal phases of the obtained powder from the precipitation method, e.g. calcined temperature, temperature and pH value as well as the stirring time of the reaction mixture, were investigated. A 99% purity of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck), a 99% purity of $(\text{NH}_4)_2\text{HPO}_4$ (Riedel-de Hain) were used as a calcium source and phosphate source, respectively. Tables 2.1 and 2.2 show the composition analysis of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$.

A Philips diffractometer, using Copper K α radiation at 30 mA and 40 KV and nickel filter, was used to identify the crystal phases of the precipitated powders obtained under various conditions. Scans were performed between 2θ value of 18° and 54° at rate $2^\circ/\text{min}$. X-ray diffraction patterns (XRD patterns) of precipitated powders obtained from unboiled and 10 min-boiled reaction mixture in which its pH value was brought up to 11 to 12 and calcined at 240° are shown in Fig.2.6 along with the typical XRD pattern of HAp powder. As can be seen in Fig.2.6, the initial solid phases, from both boiled and unboiled reaction mixture, were non-crystal (amorphous) and could not be distinguished. When both of them were calcined at 800°C for 1 h, the non-crystalline phase have been converted to crystalline phase (Fig.2.7)

It can be seen that the crystalline phase of the powders obtained from the unboiled mixture is different from that of the typical HAp. HAp was formed only in the reaction mixture that was boiled. However, there are the extra peaks for α and $\beta\text{Ca}_3(\text{PO}_4)_2$ at $2\theta = 30.7^\circ$ and 31.0° respectively. Therefore, there would be a minor presence of α and β tricalcium phosphate in the powder.

According to the above XRD results, we learnt that HAp was formed if the reaction mixture was boiled. In the next exploratory investigation, we investigated if it was important to maintain pH value of the reaction mixture to a constant value at all time. Fig. 2.8 shows the XRD pattern of the precipitation powder obtained from the reaction mixture which was brought

TABLE 2.1 Elemental composition in $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

ELEMENT	QUANTITY ANALYSIS (%)
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	min. 99
Fe	max. 0.005
K	max. 0.005
NH ₄	max. 0.005
Ba	max. 0.005
Mg	max. 0.01
Na	max. 0.01
Sr	max. 0.01
Pb	max. 0.0005
Cl	max. 0.002
PO ₄	max. 0.001
SO ₄	max. 0.002

TABLE 2.2 Elemental composition in $\text{Ca}(\text{NH}_4)_2\text{HPO}_4$

ELEMENT	QUANTITY ANALYSIS (%)
$\text{Ca}(\text{NH}_4)_2\text{HPO}_4$	min. 99
Cl	max. 0.0005
NO_3	max. 0.001
SO_4	max. 0.004
Pb	max. 0.0005
As	max. 0.001
Fe	max. 0.001
Na	max. 0.001

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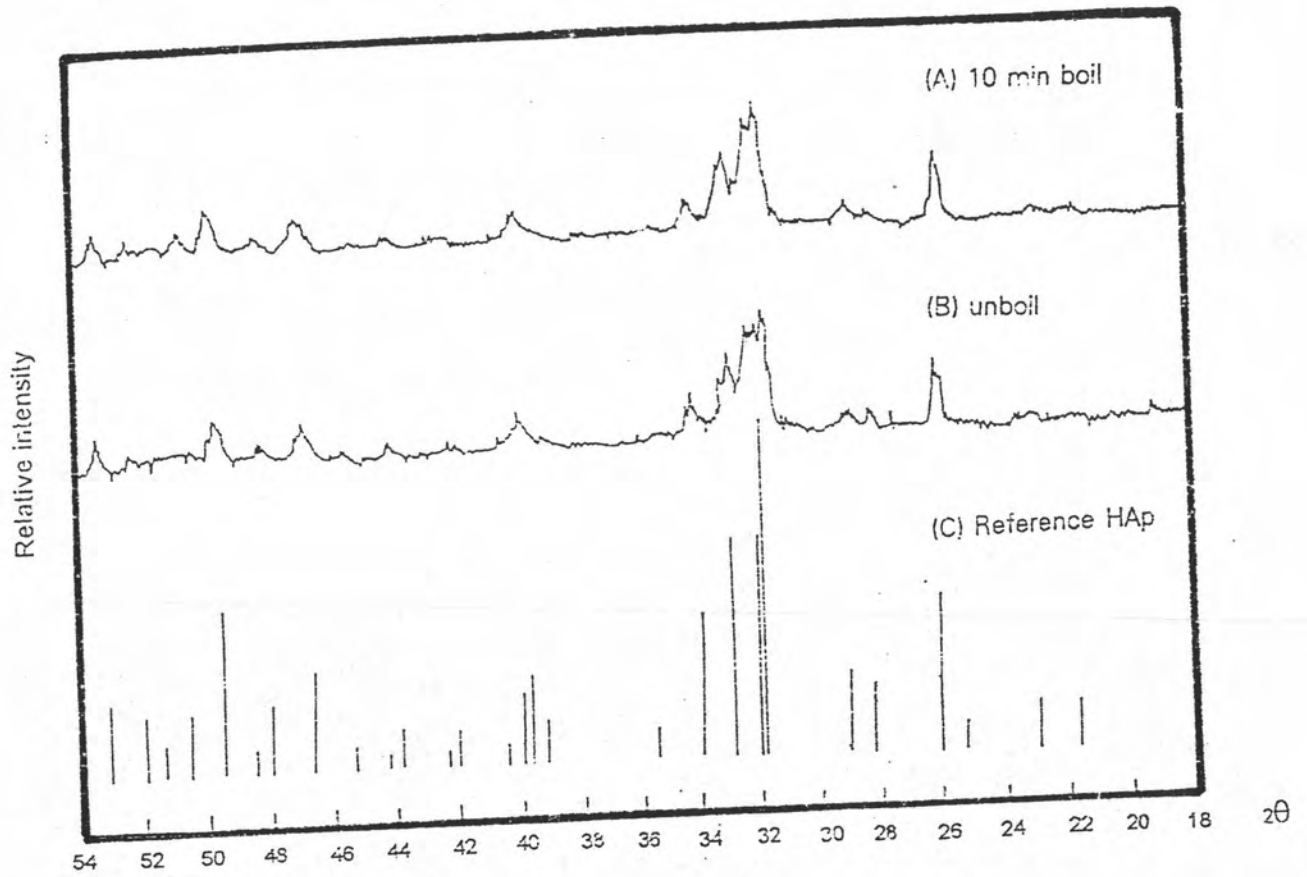


Fig.2.6 XRD patterns of 240 °C calcined HAp, obtained from reaction mixture of various temperatures, showing in comparison with reference HAp. (A) 10 min boil, (B) unboil, (C) reference HAp.

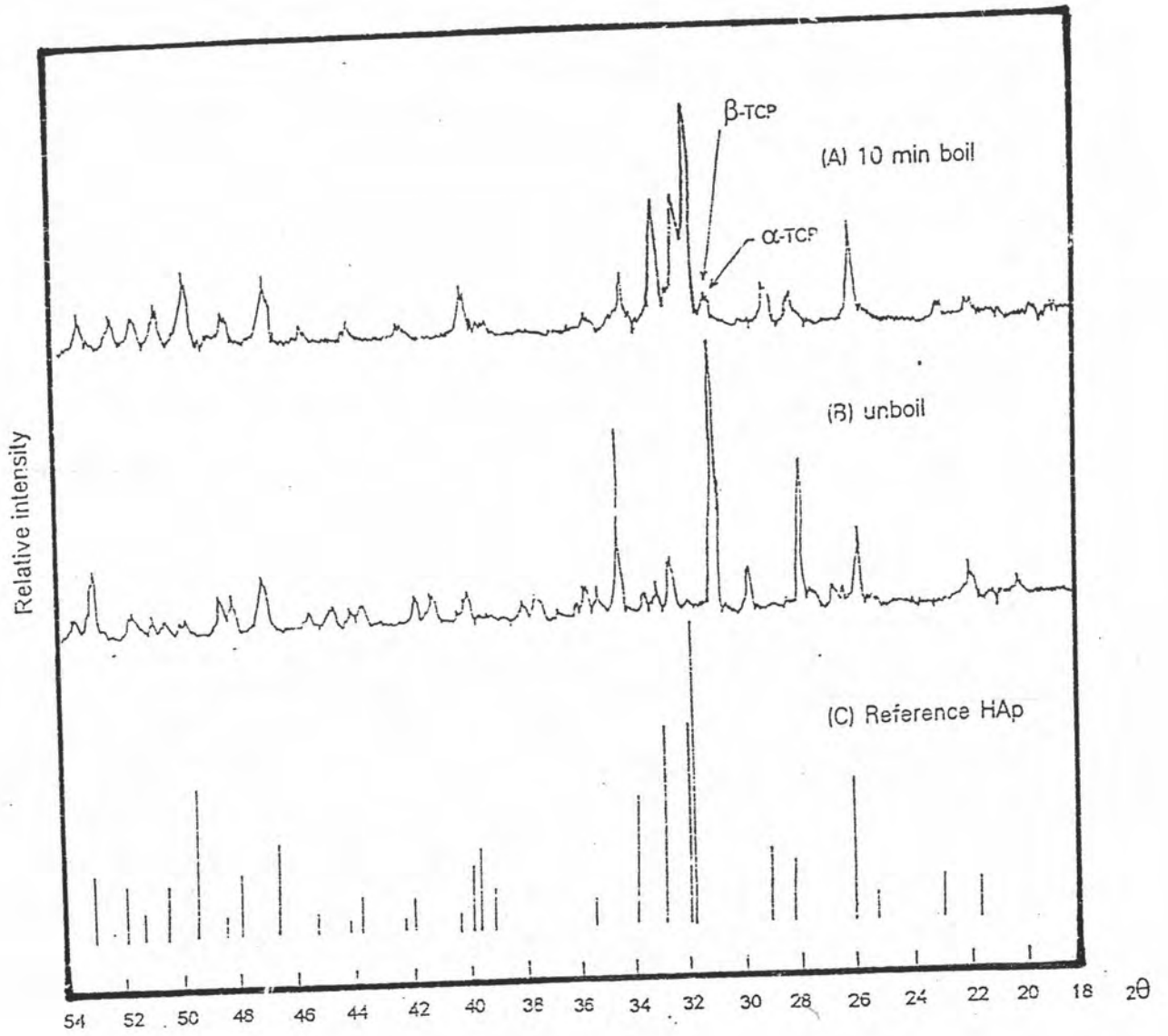


Fig.2.7 XRD patterns of 800 °C calcined HAp, obtained from reaction mixture of various temperatures, showing in comparison with reference HAp.
(A) 10 min boil, (B) unboil, (C) reference HAp.

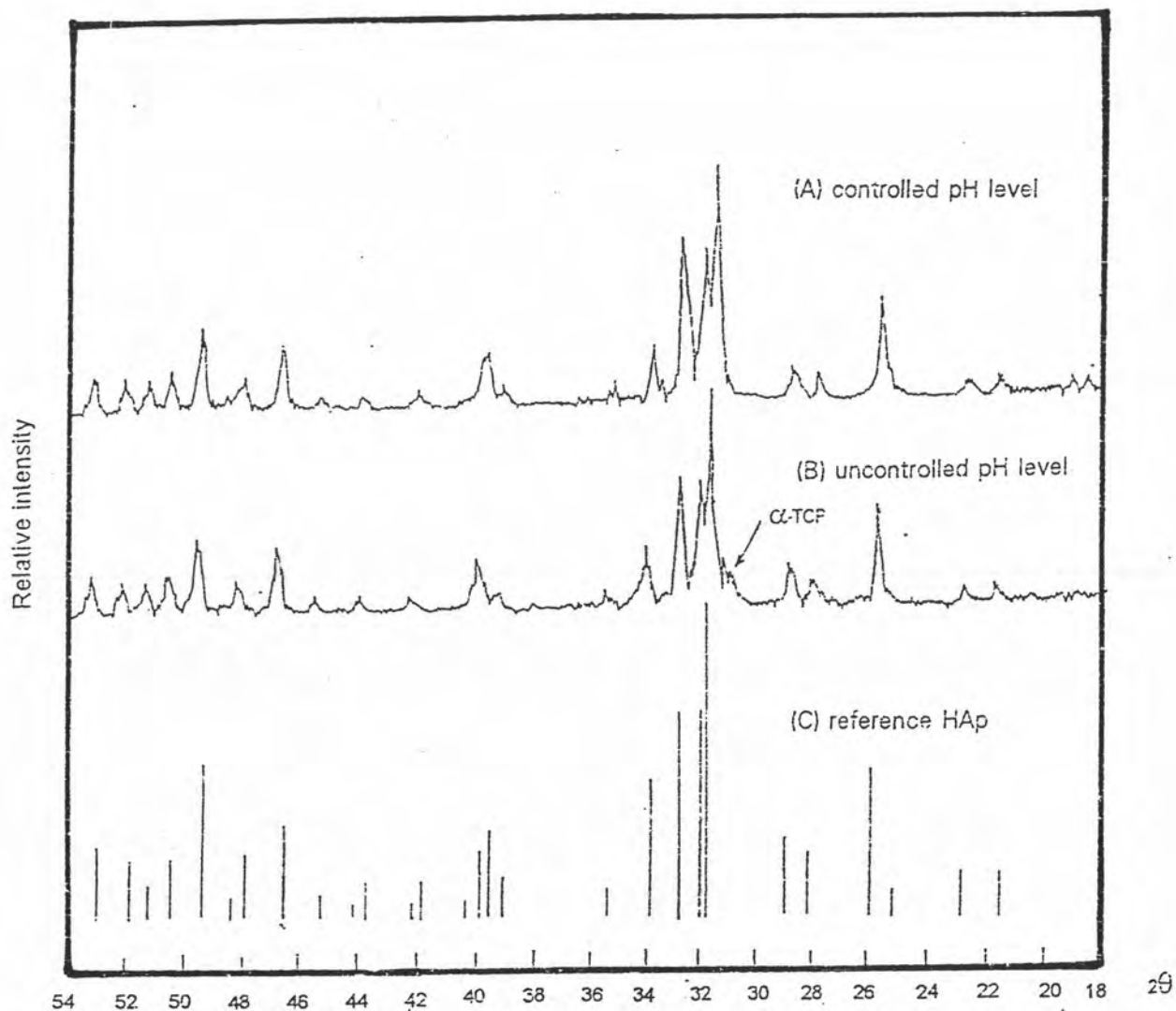


Fig.2.8 XRD patterns of 800 °C calcined HAp, obtained from 10 min boil reaction mixture with various conditions of pH level control, showing in comparison with reference HAp,

(A) pH level maintained at value of 11-12 at all time, (B) pH level adjusted to value of 11-12 only at the beginning of the reaction, (C) reference HAp.

up to pH value 11 to 12 only at the beginning of the reaction process and the XRD pattern of those obtained from the reaction mixture in which care was taken to keep its pH value to 11 to 12 at all time. Again both of the obtained XRD patterns are shown along with the typical XRD pattern of HAp. The XRD patterns of powders in Fig 2.8 indicate that the crystalline phase for both uncontrolled and controlled are all HAp. However, HAp was converted to α -Ca₃(PO₄)₂ under the condition where the phi level of the reaction mixture was not controlled, whereas the conversion did not occur for the condition where the pH value was carefully controlled to 11 to 12 at all time before boiling the reaction mixture.

Investigations were made of the effect of stirring time after the last drop of the (NH₄)₂HPO₄ solution was added. The pH value of the reaction mixture was kept to pH 11 to 12 at all time in each preparation run and the reaction mixture was boiled for 10 min for every run. The obtained XRD patterns of precipitated powders obtained from the reaction mixture subjected to four different stirring times shown in Fig. 2.9 indicate that the powders were not decomposed into α -Ca₃(PO₄)₂ if the stirring was kept long enough. The stirring time of 3.5 h was chosen in our powder preparation process.

It should be noted that the results from XRD pattern indicate that the structure of the synthesized powder was the apatite structure. However, it should be further verified that if the existence of OH⁻ vacancies occurs in its structure. The IR spectra of synthesized powders ; pH 11 - 12, stirring time 3.5 h, boiling time 10 min, is shown in Fig. 2.10 . The obtained spectra have the peaks relevant to the bonds of the phosphate ion (PO₄³⁺) around 600 and 1040 to 1100 cm⁻¹. The peaks around 3537 and 635 cm⁻¹ are due to the OH⁻ stretching vibration mode and the OH⁻ librational vibration mode, respectively. Another small peaks at around 1600 and 3400 cm⁻¹ are relevant to water. It can be seen that the IR spectra of the prepared powders correlated closely with that of reference HAp.

2.2.3 The Employed Synthesizing Procedure

The results obtained in the exploratory tests lead to the synthesizing procedure employed in our work as summarized in the flow chart showing in Fig. 2.11

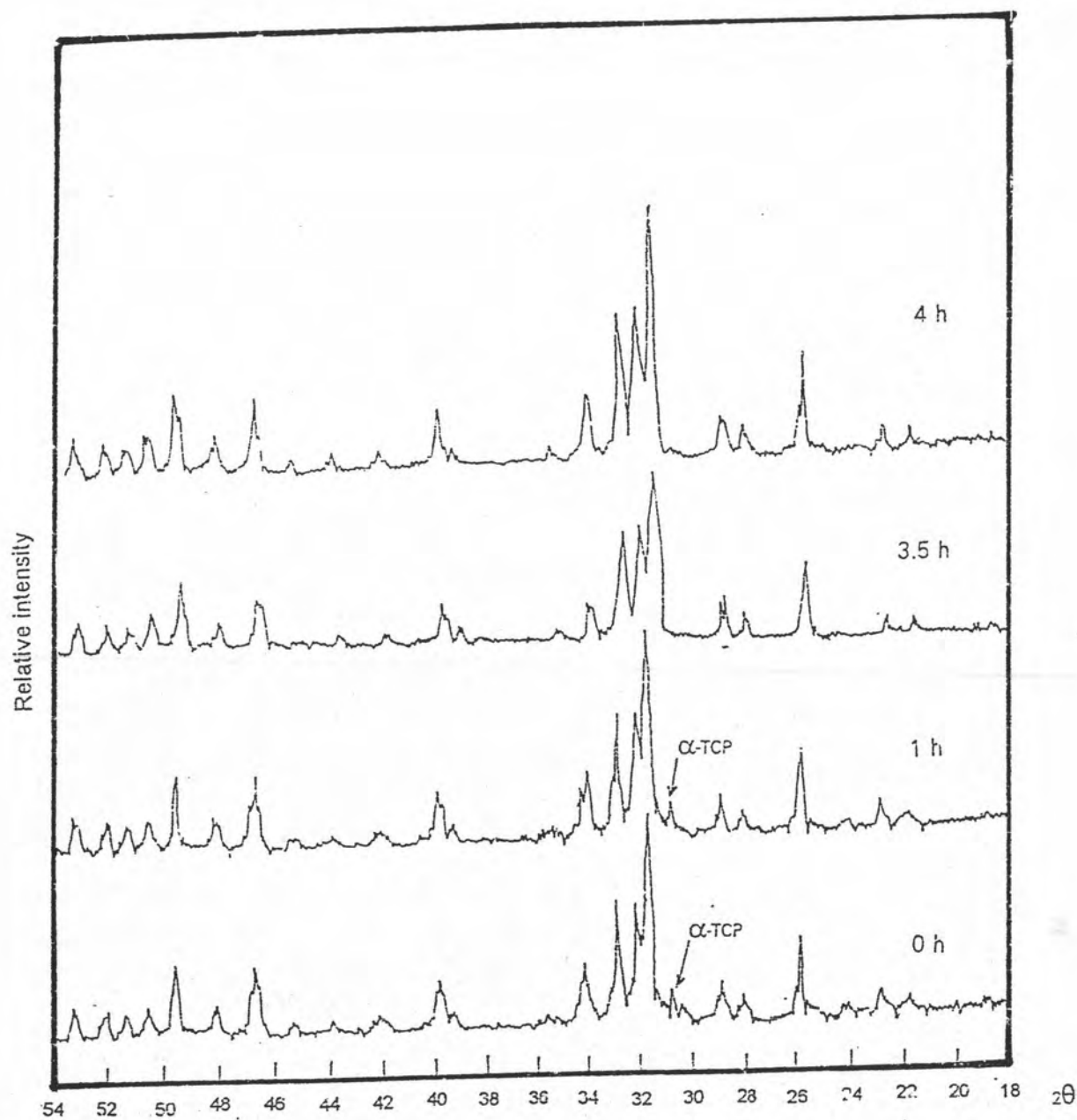


Fig.2.9 XRD patterns of 800°C calcined HAp, obtained from 10 min boil reaction mixture stirred for various length of time.

(A) stir for 4 h., (B) stir for 3.5 h., (C) stir for 1 h., (D) unstir.

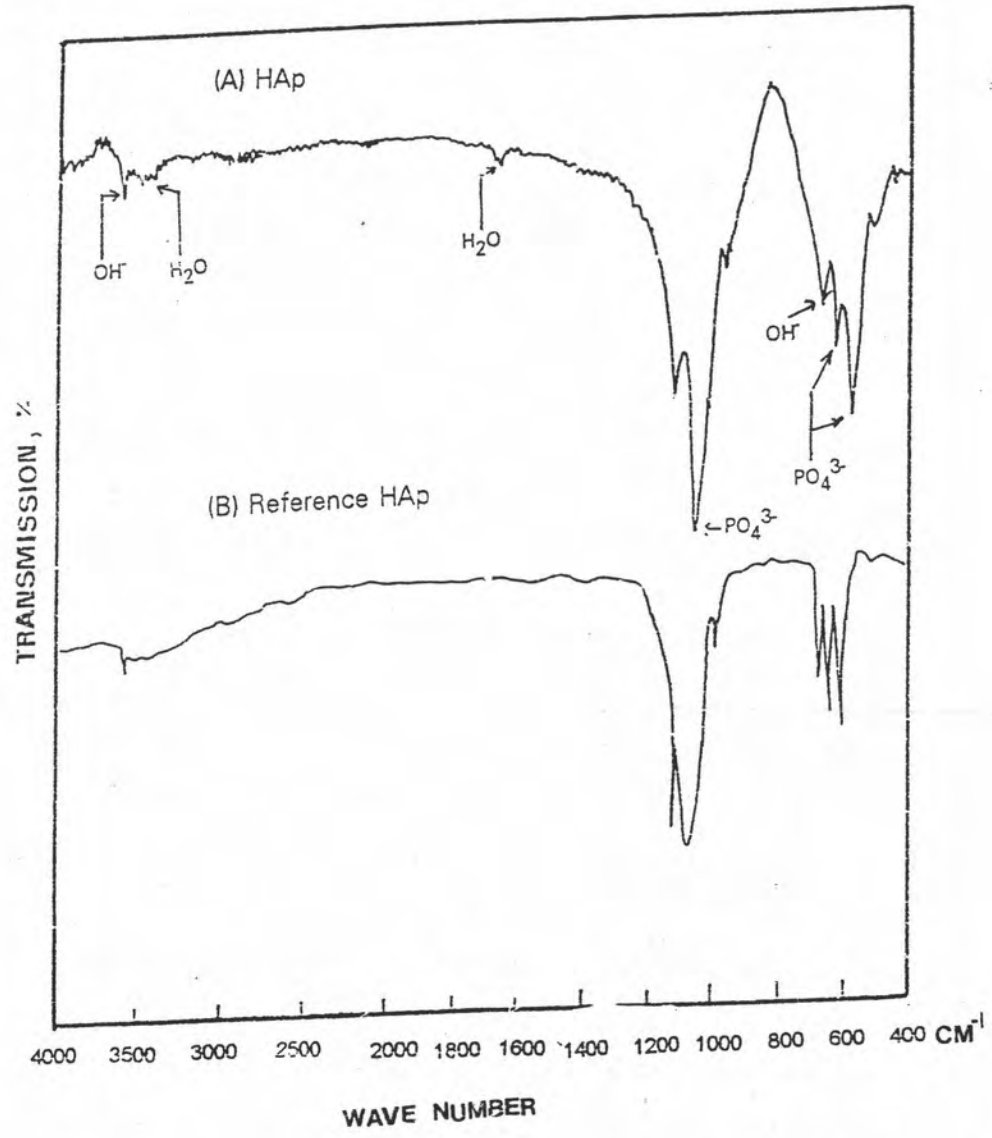


Fig.2.10 IR spectra of 800°C calcined HAp showing in comparison with reference HAp. (A) synthesized HAp, (B) reference HAp.

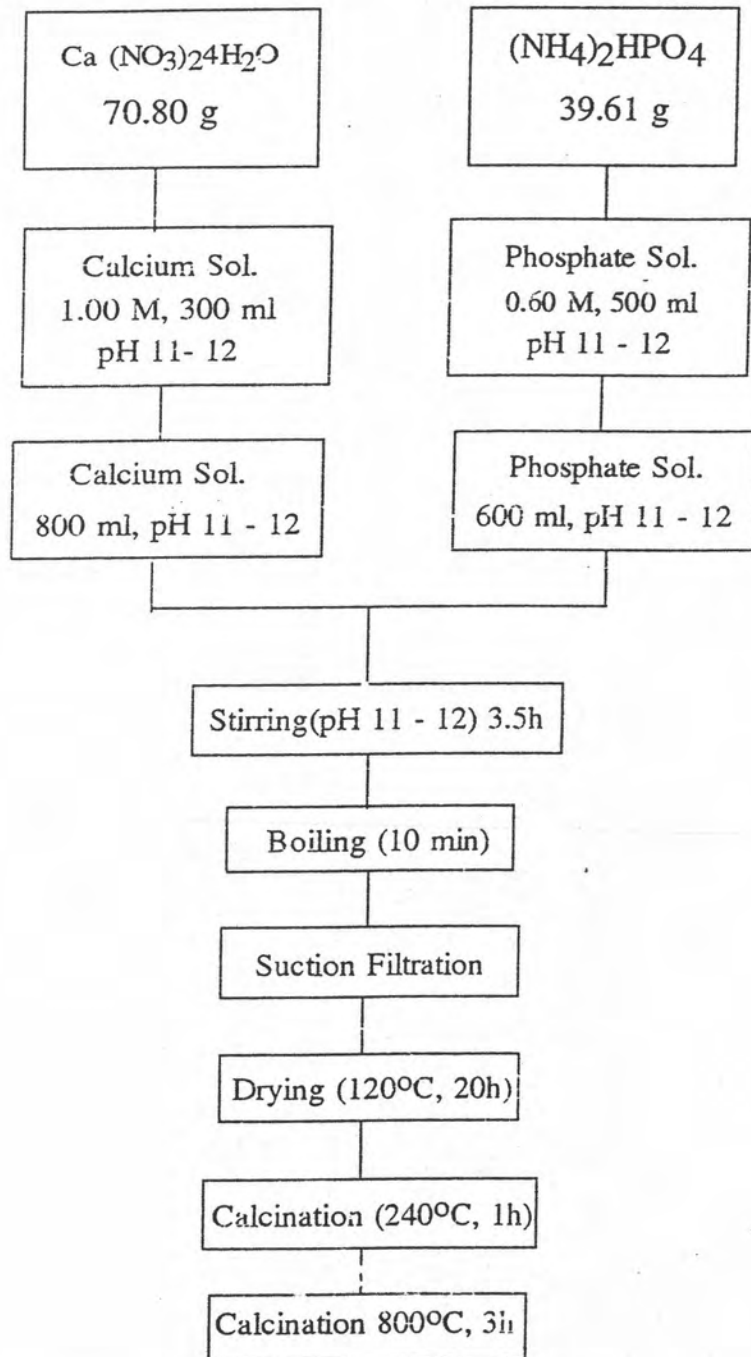


Fig.2.11 Flow chart for the synthesizing procedure employed in this work.

A solution of 1.00 M $\text{Ca}(\text{NO}_3)_2$ in 300 ml. in distilled water was prepared and brought to pH 11 to 12 with concentrated NH_4OH and finally diluted to 600 ml. A solution of 0.60 M $(\text{NH}_4)_2\text{HPO}_4$ in 500 ml. distilled water was prepared and brought to pH 11 to 12 with concentrated NH_4OH and thereafter diluted to 800 ml. The pH was checked again and additional concentrated NH_4OH was added if necessary. The pH of the solution was measured using a pH test paper. The calcium solution was vigorously stirred at room temperature, and the phosphate solution was slowly dropwise over 30 min. from a pipet into the stirred calcium solution (Fig. 2.12).

The reaction mixture, which was milky, was continuously stirred at room temperature for another 3.5 h and thereafter was boiled for 10 min and left overnight at room temperature to allow the gelatinous precipitate to settle. The pH of the reaction mixture was checked at all time and additional concentrated NH_4OH was added if necessary to maintain its pH value to 11 to 12 at all time. The resulting milky solution was suction filtered on a Buchner funnel with the application of mild suction (Fig. 2.3). The filtered cake was oven dried at 120°C for 20 h, then broken down by crushing in a mortar. The powder was calcined at 240°C for 1 h to eliminate NH_4NO_3 and was heated to 800°C for 1 h to promote powder crystallinity. The powders were broken down by crushing again if the powder agglomerated.

2.3 Compacting and Sintering

The calcined powders were dry milled for 60 h in a rotating urethane liner steel jar with alumina balls (9.62 mm. in diameter) to break agglomerates and reduce the powder sizes. Batches of powder (≈ 2.5 g/batch) were single-end die press to 3 MPa using a high-purity graphite die, punch and spacer assembly. The resulting powder compact was disc shape ; 25 mm. diameter and 2.42 mm. thickness (Fig 2.13). Remove of any defects associated with die pressing was achieved by subsequent wet-bag isostatic pressing at 250 MPa.

Green discs were packed in a high-purity alumina crucible for firing with the heating rate of $100^\circ\text{C}/\text{h}$ from room temperature to a sintering temperature of 1200°C . The temperature was

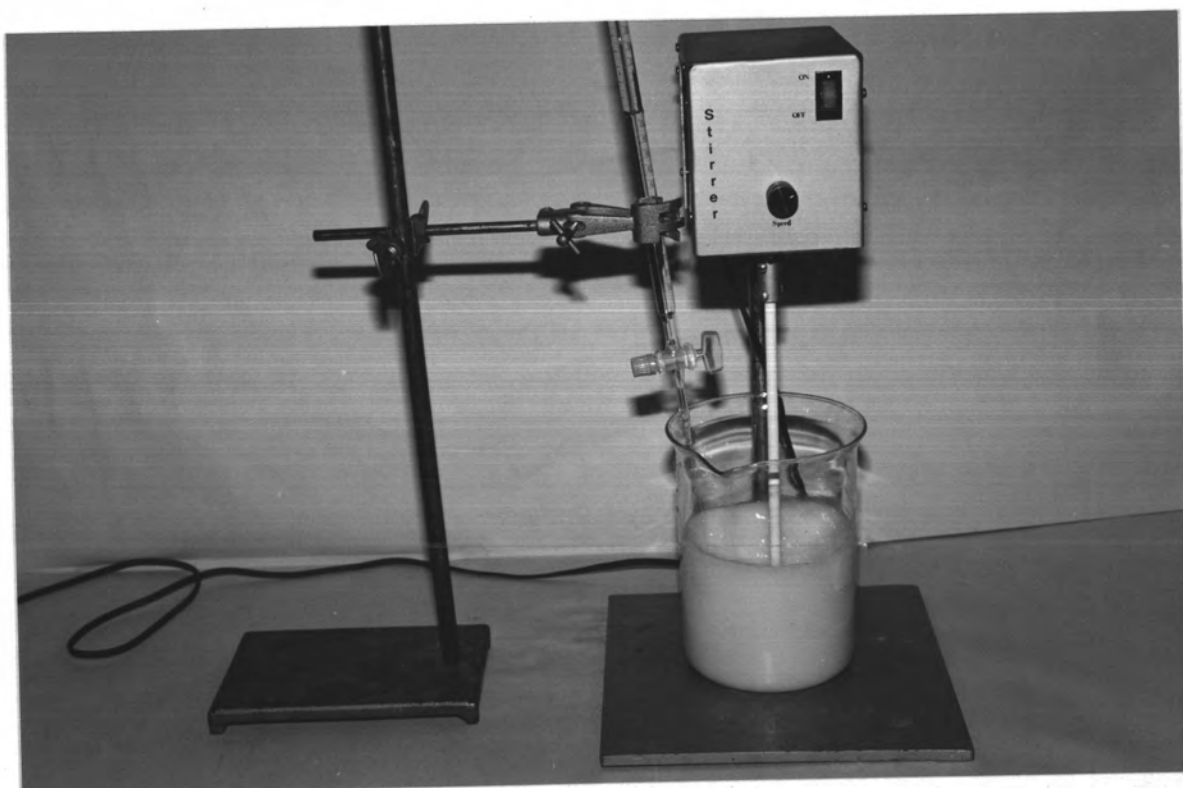


Fig.2.12 Photograph of the experimental set up of HAp synthesis through precipitation reaction.

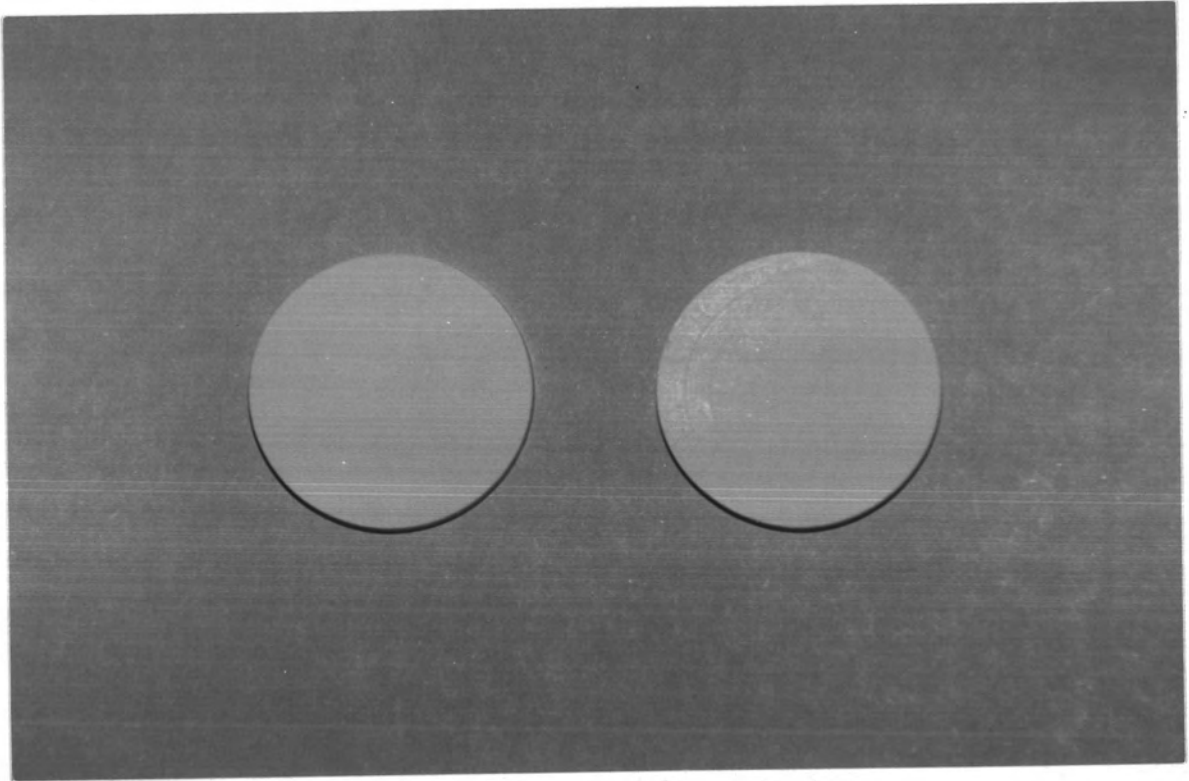


Fig.2.13 Photograph of compacted HAp specimens.

kept constant at 1200°C for 1 h. Specimens were cooled at 100°C/h. The heat treatments were carried out in air using a box furnace.

2.4 Characterization

2.4.1 X-ray Diffraction

The sintered specimens were crushed to fine powders and examined crystal phases in a Philips diffractometer using copper K α radiation at 30 mA and 40 KV, and Nickel filter. A time constant of 1 s and a scanning rate of 2°min⁻¹ were used. The XRD patterns were recorded with a chart drive speed of 2 cm min⁻¹ and the 2θ values were varied from 18° to 52°.

2.4.2 Infrared Absorption

The infrared (IR) absorption spectra of the sintered specimen was crushed and examined by a fourier transform infrared spectrophotometer (FTIR). The IR spectra were recorded with wave number varied from 4000 to 400 cm⁻¹.

2.4.3 Specimen Density

Density of the specimens were determined by the Archimedes method using distilled water as the immersion medium. The procedure is as follows :

1. Test specimens were dried to constant weight by heating in an oven to 110 °C and the dry weight, D , was determined.
2. Test specimens were placed in water and boiled for 2h. care was taken that the specimens were covered with water at all time. Then the specimens were immersed in water for 20h before weight and the weight, s , was determined. This weight was accomplished by suspending the specimen in a loop of copper wire hung from one of the balance and immersed in water.
3. After determining the suspended weight, each specimen was blotted lightly with a moistened cotton cloth to remove all drops of water from the surface and the saturated weight, w , was determined by weight in air.

4. Bulk density was determined from the quotient of its dry mass (D) divided by the exterior volume, including pores $B=D/(W-S)$.

2.4.4 Powder Morphology

Scanning electron microscope (SEM) (JEOL : JSM-T220A) was employed to investigate the morphology of the obtained powders. The powders were coated with a thin layer of gold before being observed by the SEM.

2.4.5 Specimen Microstructure

Specimen surfaces were polished for optical and scanning electron microscopy with a series of grit size of SiC paper (800 , 1200 μm) and alumina pastes (1, 0.25, 0.03 μm). Microstructure were revealed by a thermal etching at 1180°C for 10 min in air. After the thermal etching, the surfaces were coated with a thin layer of gold. Microscopic examinations were made by reflected-light microscopy and scanning electron microscopy .

2.5 Results

2.5.1 X-ray Diffraction

The XRD pattern of the powders crushed from the fabricated specimens is shown along with that of the typical HAp in Fig. 2.14 . It can be seen clearly that the XRD peaks of sintered specimen correlated closely with the reference HAp and the peaks of α -TCP and β -TCP phase were not occurred in these specimens [α -TCP : $2\theta = 30.7^\circ$, β -TCP: $2\theta = 31.0^\circ$]. It was therefore concluded that the crystal structure of sintered specimen was the apatite structure.

2.5.2 Infrared Spectra

The infrared absorption spectra of the sintered specimens is shown along with that of the reference HAp in Fig. 2.15. The sharp peak at 3537 cm^{-1} was assigned to OH⁻

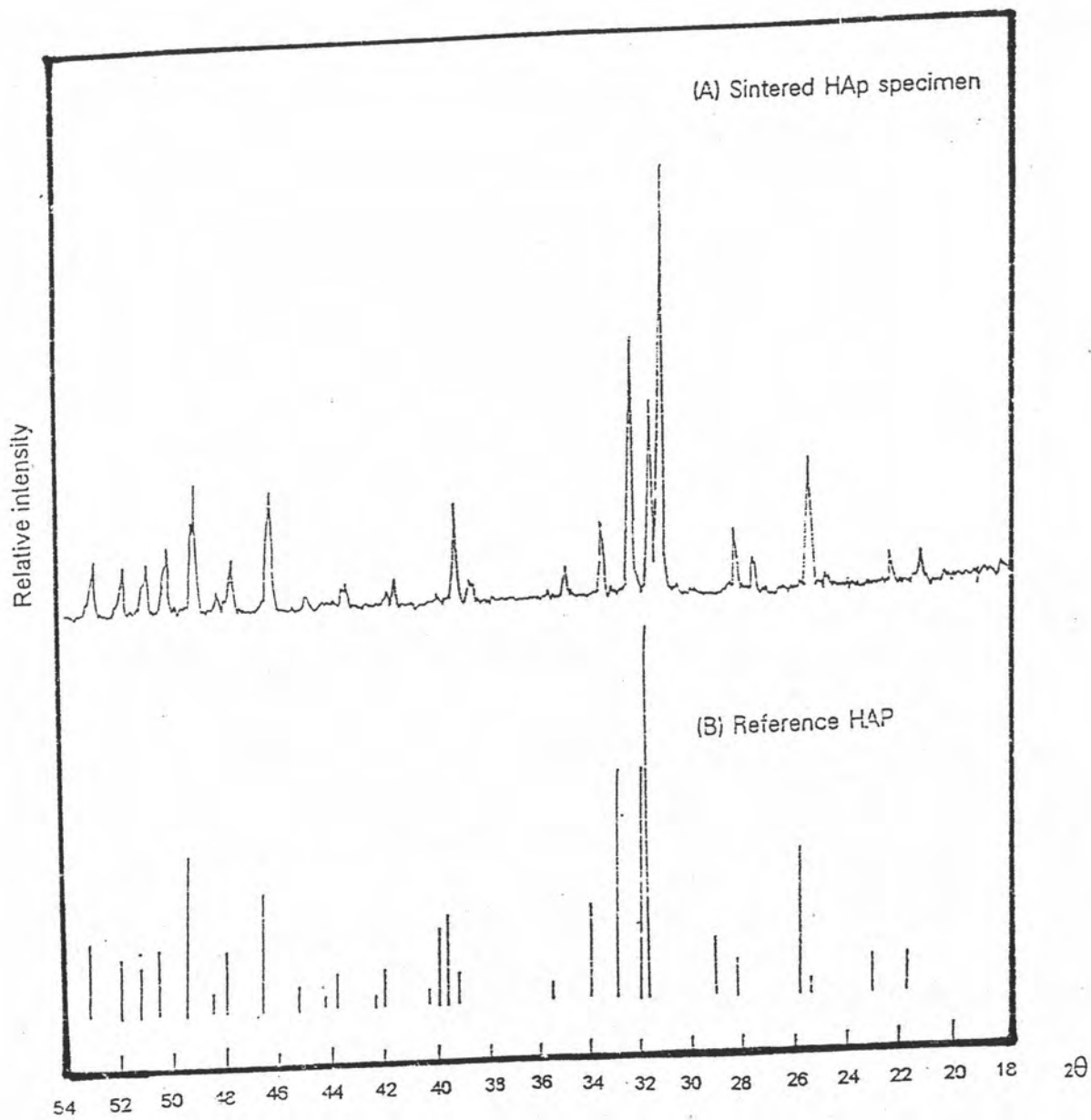


Fig.2.14 XRD patterns of 1200°C sintered HAp specimen showing in comparison with reference HAp.

(A) sintered HAp specimen, (B) reference HAp.

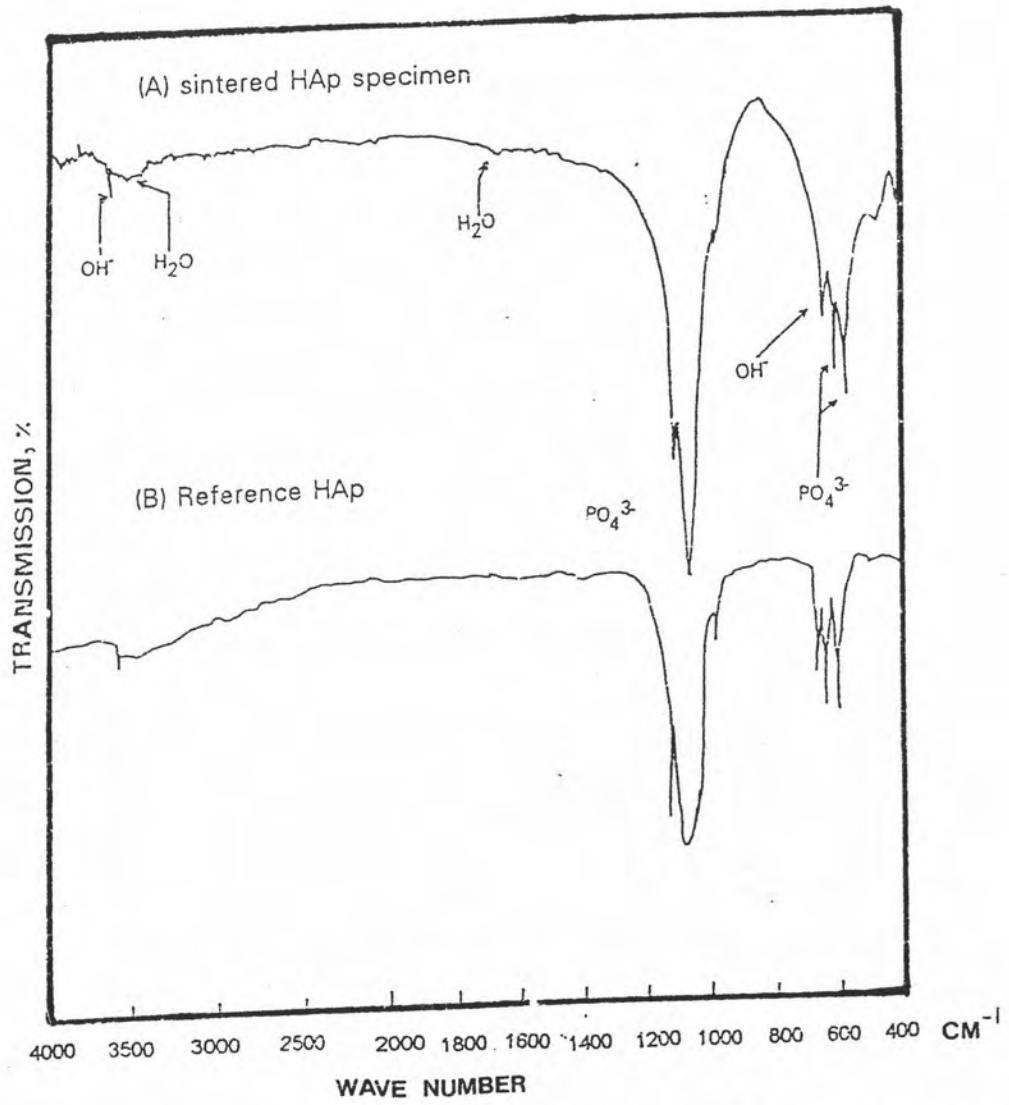


Fig.2.15 IR spectra of 1200°C sintered HAp specimen showing in comparison with reference HAp.

(A) sintered HAp specimen, (B) reference HAp.

stretching vibration mode. Peaks at 635 cm^{-1} was assigned to OH^- librational vibration mode and peaks at around 600 and 1040 to 1100 cm^{-1} were assigned to PO_4^{3-} . The small peaks at around 1600 and 3400 cm^{-1} were relevant to water (H_2O). The IR spectra of sintered specimen correlated to reference HAp so it indicates that there is no OH^- loss that lead to requiring for OH^- vacancies in the HAp structure.

2.5.3 Specimen Density

The theoretical density of HAp is 3.16 g/cm^3 . Density of the sintered specimen was found to be 3.11 g/cm^3 . So the relative density of sintered specimen was 98% of the theoretical density indicating that the sintering was quite well completed at this sintered temperature of 1200°C .

2.5.4 Powder Morphology and Microstructure

Fig. 2.16 shows the SEM micrograph of the synthesized powders. It indicates that the synthesized powders are mostly agglomerated. The estimation of the agglomerated powders dimension is about $7\mu\text{m}$. The SEM micrograph of microstructure of the sintered specimen is shown in Fig. 2.17. It can be seen that the grain shape was equiaxed. The average grain size is $1.8 \pm 0.1\mu\text{m}$.

2.6 Discussion and Conclusion

Exploratory tests (Sect.2.2.2) were made in this work to investigate the effect of various parameters on the products obtained from the precipitation reaction between $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ in base medium. To successfully produce HAp powders, we have found that the following care must be taken :

(i) The pH value of the reaction mixture between $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution and $(\text{NH}_4)_2\text{HPO}_4$ solution must be kept constant at value of 11 to 12 all the time. This is because before the HAp ($\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$) could be formed, HPO_4^{2-} arising from $(\text{NH}_4)_2\text{HPO}_4$

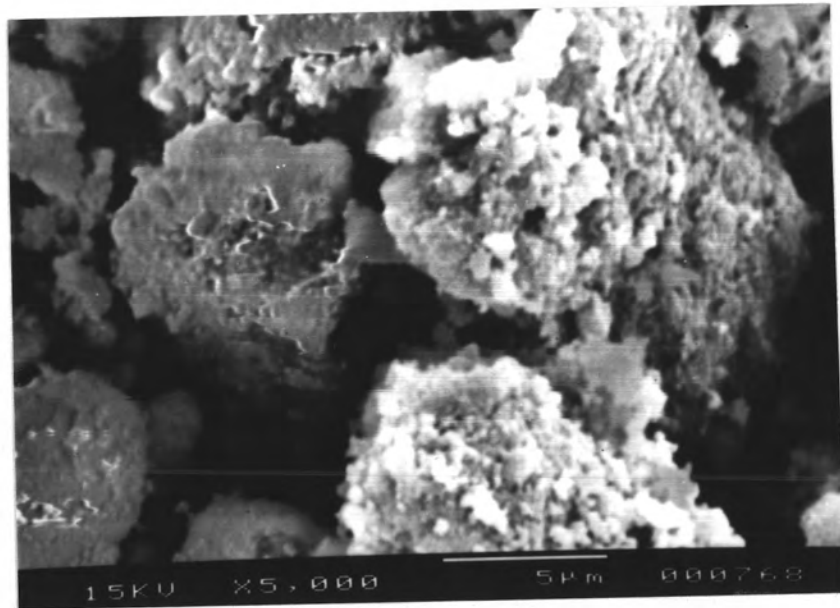


Fig.2.16 SEM micrograph of synthesized HAp powders.

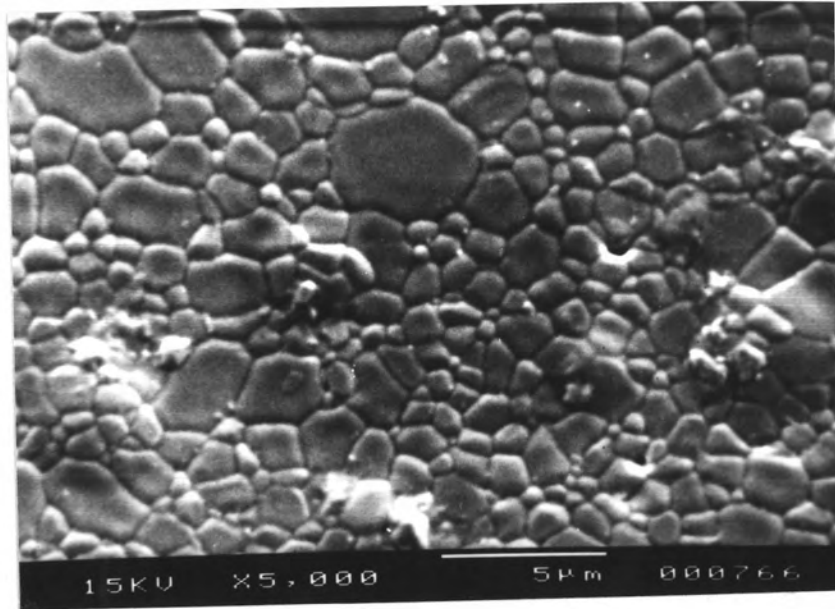


Fig.2.17 SEM micrograph of microstructure of 1200°C sintered HAp specimen.

solution must react with OH^- giving out by the addition of NH_4OH first to produce PO_4^{3-} according to the reaction



The reversibility of the above reaction could be prevented if OH^- is kept in excess by maintaining the pH level at 11 to 12 at all time. The presence of HPO_4^{2-} will cause the undesirable formation of $\text{Ca}_4\text{H}(\text{PO}_4)_3 \cdot 2\text{H}_2\text{O}$ according to reaction

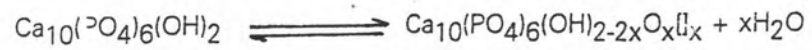


(ii) The reaction mixture must be boiled. This is because at the high temperatures, the molecules travel faster and undergo more effective collisions within a unit of time, i.e. the reaction rate, increases if the temperature of the system increases. Under these conditions, the molecules approach sufficient speed to overcome the repulsion of the respective electron clouds and new molecules can be formed(24);

(iii) The reaction mixture should be kept stirring at a sufficient length of time. We have found that if the stirring time is not long enough (less than 3.5 h) the α -TCP phase appeared in HAp matrix (Fig.2.9). This is due to the incomplete reaction between $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$.

Our established procedure for preparing HAp specimens (Sect. 2.2.3 and 2.3) has proven to be capable of producing HAp specimens which are fine grain and highly dense (Sect.2.5). The grain shape is equiaxed and grain size is $1.3 \pm 0.1 \mu\text{m}$. High density of 98% theoretical density is achieved. The problem of the thermal decomposition of HAp into α - and β tricalcium phosphate, as previously pointed out in Sect.2.1, is overcome in this work. No α or β tricalcium phosphate peaks was found in its XRD pattern (Fig.2.14) when the sintered temperature of 1200°C was employed in our work. The observed peaks at 3537 and 635 cm^{-1} in the IR spectra of our prepared specimens (Fig.2.15) indicates that after sintering at 1200°C in air there was no dehydration in our HAp specimen, which leads to the occurrence of OH^-

vacancies in the structure of HAp. Most previous works emphasize the necessities to pass water through the furnace at all time to prevent such dehydration of HAp during sintering at temperature of 1100°C to 1300°C as



Accordingly, even without damp atmosphere during firing to temperature as high as 1200°C, we are still able to preserve the structure of HAp, with no loss of OH⁻ and no minor presence of α - and β tricalcium phosphate in our prepared specimens.