Precipitation Method in Calcium Phosphat Synthesis from Blood Clamshells (Anadara Granosa)

K Nurma Wahyusi*, N Karunia, M Satrya
Chemical Engineering, Engineering Faculty, University of Pembangunan Nasional “Veteran” East Java

* kindrinurma@gmail.com

Abstract. Sources of calcium phosphate can be produced from materials containing calcium carbonate (CaCO_3). These materials are usually found in clamshells, eggshells and limestone. Calcium phosphate can be produced by chemical precipitation by reacting calcium carbonate (CaCO_3) from a material containing CaCO_3 with HCl and then reacting again with Na_2HPO_4 and calcium phosphate Ca_3(PO_4)_2 is obtained. In this study raw materials used for blood clamshells waste. Precipitation is a method which results in the formation of solids in solution or in other solids during chemical reactions. From the results of XRF analysis it can be seen that the best results entered in the classification of calcium phosphate are at pH 8 with a stirring time of 3 hours and pH 9 with a stirring time of 4 hours there is a Ca/P value of 1.5. At the Ca/P value it forms Tricalcium Phosphate. There are 3 types of Tricalcium Phosphate which are α, β and amorphous. It can be concluded that the longer the stirring time and the pH value increase, the Ca / P value also increases. To form TCP (Tricalcium Phosphate).

Keywords: Precipitation Methods, Calcium Phosphate, Blood Clamshells

1. Introduction
Indonesia, which is mostly waters, consists of various types of shells, one of which is blood clamshells (Anadara granosa). Various types of clams are generally not fully utilized, mostly only the contents of the clams are used as a protein-rich food, while the shell is discarded or only used as decoration. Even clam the shells, which are mostly composed of calcium, can be used to synthesize hydroxyapatite as a bone plate in the process of recovering bone damage. Raw materials that can be used for the manufacture of calcium phosphate most are shell waste, for example, eggshell shells, clamshells, and chitosan shells. This research was conducted in the manufacture of calcium phosphate by using raw materials of blood clamshells waste to determine the levels of calcium, phosphorus and the best quality of calcium phosphate. Therefore this can affect the alternative ingredients for making calcium phosphate using waste shells from blood clams. [12]

Waste clamshells that accumulate are a type of blood clam (Anadara granosa). Amount of clams that are quite abundant will be proportional to the amount of skin which has so far been mostly only discarded and a small portion is used as animal feed, raw materials for making cosmetics, and traditional crafts. Sea clamshells waste contains pozzolanic chemical compounds namely lime (CaO) of 66.7%, alumina, and silica compounds. Based on these chemical compounds, blood clams can be used as an alternative to the main raw material or substitute material for making calcium phosphate. Then the waste of blood clam shells can be optimized as raw material for making environmentally friendly calcium phosphate. [8]

**References**

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Blood clams have higher levels of calcium carbonate (CaCO₃) compared to limestone, eggshells, ceramics, or other materials. This can be seen from the level of violence of the shells. The harder the shell, the higher the calcium carbonate (CaCO₃) content.

### Table 1. Chemical composition of blood clam shell powder
(Anadara granosa Linn.)

| Component       | Content (% by weight) |
|-----------------|-----------------------|
| CaCO₃           | 98.7                  |
| Na              | 0.9                   |
| P               | 0.02                  |
| Mg              | 0.05                  |
| Fe, Cu, Ni, B, Zn, Si | 0.02                  |

#### 1.1. Calcium phosphate

Calcium phosphate is the name given to a family of minerals that contain calcium (Ca²⁺) ions together with orthophosphate (PO₄³⁻), metaphosphate or pyrophosphate (P₂O₇⁴⁻) and sometimes hydrogen or ions hydroxide. [1][10]

Just as the name suggests, calcium phosphate is made from a combination of calcium and phosphorus. One type of calcium phosphate, known as hydroxyapatite, is the body's main mineral used to build and strengthen bones and teeth. [4][13]

### Table 2. Types of calcium phosphate and product solubility at 25°C

| Compound                      | Compound Formula       | Ca/P | Ksp      |
|-------------------------------|------------------------|------|----------|
| Mono calcium phosphat monohydrate | Ca(H₂PO₄)₂·H₂O         | 0.5  | High Solubility |
| Mono calcium phosphat anhydride | Ca(H₂PO₄)₂         | 0.5  | High Solubility |
| Calcium hydrogen anhydrous phosphate | CaHPO     | 1    | 10⁻⁶.90  |
| Calcium hydrogen phosphate dihydrate | CaHPO₂H₂O     | 1    | 10⁻⁶.59  |
| Tricalcium phosphate         | Ca₃(PO₄)₂         | 1.5  | 10⁻²⁸.⁹  |
| Tricalcium phosphate         | Ca₃(PO₄)₂         | 1.5  | 10⁻²⁵.⁵  |
| Amorphous calcium phosphate  | Ca₃(PO₄)₂         | 1.5  | 10⁻²⁵.²-10⁻²⁴.⁸ |
| Hydroxyapatite               | Ca₁₀(PO₄)₆(OH)₂ | 1.67 | 10⁻¹⁶.₈  |
| Tetra calcium phosphate      | Ca₄(PO₄)₂O        | 2    | 10⁻³₈    |
| Octa calcium phosphate       | Ca₈H₁₀(PO₄)₆·5H₂O | 1.33 | 10⁻₉₆.₆  |

#### 1.2. The content and benefits of calcium phosphate

Of the basic composition of the human body, calcium ranks fifth after oxygen, carbon, hydrogen and nitrogen, and weighs 1.9% of the weight of the human body. Calcium phosphate plays an important role in the physiology and biochemistry of organisms and cells. Neuromuscular function, helps the enzymes process, blood clotting, and gives strength to the framework based on phosphate salt bonds. Many enzymes that require calcium as a cofactor, for example, are in the process of blood clotting. And also helps the health of the teeth. [11]

In theory, sources of calcium phosphate can be produced from materials containing calcium carbonate (CaCO₃). These materials are usually found in shells, eggshells and limestone. Calcium phosphate can be produced by chemical precipitation by reacting calcium carbonate (CaCO₃) from a material containing CaCO₃ with HCl and then reacting again with Na₂HPO₄ and getting precipitated calcium phosphate Ca₃(PO₄)₂.
1.3. Precipitation

Precipitation is the reaction of the formation of solids in a solution as a result of chemical reactions. This precipitation is usually formed when the concentration of dissolved ions has reached the limit of solubility and the result is forming salt. In Chemistry, precipitation briefly means precipitation. It can also be interpreted as an event of precipitating or decreasing an ingredient or substance in solution due to a chemical reaction. These precipitation events can be accelerated by reducing solvent levels or adding precipitation agents. [3]

Precipitation is a method which results in the formation of solids in solution or in other solids during chemical reactions. Precipitation can also occur due to diffusion in solids. Chemicals that cause solids are called setters. Without the strength of enough gravitational energy to bring solid particles down together, the sediment will remain as a suspension.

The selected synthesis process is the precipitation process, in which the process is an acid-base reaction which produces crystalline solids (the reaction salt) and water. Some reasons for choosing this process are cheap raw materials, relatively simple chemical reactions and the size and homogeneity of the obtained particle sizes tend to be quite good. The reaction mechanism happens:

\[
\begin{align*}
\text{CaCO}_3(s) & \quad + \quad 2 \text{HCl}(l) \quad \rightarrow \quad \text{CaCl}_2(l) \quad + \quad \text{CO}_2(g) \quad + \quad \text{H}_2\text{O}(l) \\
3 \text{CaCl}_2(l) & \quad + \quad 2 \text{Na}_2\text{HPO}_4(s) \quad \rightarrow \quad \text{Ca}_3(\text{PO}_4)_2(aq) \quad + \quad 4 \text{NaCl}(aq) \quad + \quad 2 \text{HCl}(l)
\end{align*}
\]

The size, shape, and surface of the Tricalcium phosphate particles obtained with this reaction are very sensitive to the rate of sodium phosphate addition and the temperature of the reaction. The rate of addition of sodium phosphate is closely related to the pH obtained at the end of synthesis and also to the stability of the suspension.[2][5]

1.4. The factors that influence the formation of tricalcium phosphate in this method are as follows:

- **Stirring**
  In this method, inadequate stirring will cause the formation of unwanted phases, namely monetite (CaHPO₄) and brushite (CaHPO₄.2H₂O). Also sufficient stirring will contribute to better pH control of the mixture and lead to better interactions between reagents.

- **pH**
  In this method the control of pH is very important because it is a parameter that greatly influences the value of the Ca/P ratio. The pH value must be controlled effectively, if not, at a pH lower than 7 there will be formation of calcium monophosphate and dehydrated calcium which is quite soluble in the water medium. The degree of pH also affects the level of purity and morphology of Tricalcium phosphate crystals that are formed.

- **Temperature**
  With increasing sintering temperature more calcium phosphate compounds are produced. The increase in crystallinity is shown by an increase in peak intensity and directly varies with an increase in temperature.

- **The rate of addition of sodium phosphate**
  The low rate of addition of sodium phosphate will result in large crystallite sizes. [7]

2. Research Methods

2.1. The procedure in this study can be explained as follows:

The shells of the blood shells are washed clean so that there is no dirt attached, then dried in the sun for 2 days. After drying, the shelling of blood clams is done up to 100 mesh, beaker glass containing 2 N hydrochloric acid as much 200 ml, and added solids shells 20 grams, then stirring for the specified stirring time variable (1, 2, 3, 4, and 5 hours). Then the filtering is done, the filtrate is separated from the impurities in the filtrate.

After that the addition of Na₂HPO₄ with a concentration of 3 N until it reaches the desired pH (6, 7, 8, 9, 10) and the filtrate and sediment are separated again. Then the Ca₃(PO₄)₂ precipitate is obtained, the precipitate is put into the furnace for 2 hours at 900 °C, the calculation of the solids obtained from the shells of the shells and analysis of the composition of Ca and P in the shells of the shells.
2.2. Results of XRF Analysis of Calcium Phosphate

To find out the composition of calcium phosphate content, XRF analysis test is needed, the results obtained are the characteristics of TCP (Tricalcium Phosphate).

The analysis used in this study is X-Ray Fluorence (XRF) analysis. XRF is a tool used to analyze the chemical composition and the concentration of elements contained in a sample by using the spectrometry method. XRF is commonly used to analyze elements in minerals or rocks. Elemental analysis is done both qualitatively and quantitatively. Qualitative analysis is done to analyze the types of elements contained in materials and quantitative analysis is carried out to determine the concentration of elements in materials. The principle of XRF is If there is excitation of primary X-rays coming from X ray tubes or radioactive sources regarding the sample, X-rays can be absorbed or scattered by the material. The process by which X-rays are absorbed by atoms by transferring energy to electrons in deeper skins is called the photoelectric effect.

During the process, when the primary X-rays have enough energy, electrons move from the inner skin causing a vacuum. This vacuum results in an unstable atomic state. When the atom returns to a stable state, electrons from the outer shell move to the deeper skin and this process produces a certain X-ray energy and is different between the two bonding energies in the skin. X-ray emissions are produced from a process called X Ray Fluorescence (XRF). The process of detecting and analyzing X-ray emissions is called XRF analysis. [9].

3. Result and Discussion

From Fig 1. It can be seen that the Ca / P value of the five stirring times of 1-5 hours has increased with increasing pH. In this method the control of pH is very important because it is a parameter that greatly influences the value of the Ca / P ratio. The pH value must be controlled effectively, if not, at a pH lower than 7 there will be formation of calcium monophosphate and dehydrated calcium which is quite soluble in the water medium. The degree of pH also affects the level of purity and morphology of TCP crystals that are formed. [9]

At pH 6 the Ca / P value was obtained with a stirring time of 1 hour of 0.4, then at the stirring time of 2 hours the value of Ca / P was 0.96, at a stirring time of 3 hours the Ca / P value was 1, at a stirring time of 4 hours the Ca / P value was 1.2, and at the stirring time 5 hours the Ca / P value was 1.6. From the graph above it can be seen the value of Ca / P produced has increased in every variable pH 6 to pH 10. This happens because when the pH increases, the mass of the product calcium phosphate also increases. Because this cause is what makes the value of Ca / P contained in the product yield is also greater. However, in this graph the best Ca / P values can occur at pH 8 with a stirring time of 4 hours, and at pH 9 with a stirring time of 3 hours, because at the time of the pH and the stirring time, α, β, and Tricium Phosphate are formed. amorphous that is with an exact Ca / P value of 1.5
4. Conclusion

The conclusions for this research are as follows:

Tricalcium phosphate (TCP) as a bone replacement biomaterial can be made from natural ingredients. Blood shells that contain lots of calcium can be a precursor in making TCP. The making of TCP from blood clam shells can be obtained by reacting calcium from blood clam shells with HCl and Na2HPO4 by precipitation methods with a sintering temperature of 900 °C. From the results of XRF characterization, it can be seen that the best results entered in the classification of calcium phosphate are at pH 8 with a stirring time of 3 hours and pH 9 with a stirring time of 4 hours ie a Ca / P value of 1.5. in these circumstances the value of Ca / P forms Tricalcium Phosphate. There are 3 types of Tricalcium Phosphate which are α, β and amorphous. It can be concluded that the longer the stirring time and the pH value increase, the Ca / P value also increases. To form TCP (Tricalcium Phosphate).

5. References

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