# PREPARATION OF CALCIUM-POTASSIUM-PHOSPHORUS (Ca-K-P) AS A MATERIAL FOR SOIL AND PLANT IMPROVEMENT USING THE PRECIPITATION METHOD

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**Abstract**

Calcium carbonate ($CaCO_3$) is a material that is widely found in Indonesia, both in the form of rocks and in various types of shell waste. This study utilizes $CaCO_3$ rocks as a source of CaO for the manufacture of calcium-potassium-phosphate (Ca-K-P) composites using the precipitation method. Ca-K-P composites can be used to improve the quality of acidic soil, roots and plant quality due to the presence of calcium (Ca), potassium (K) and phosphorus (P). The phosphorus element is the result of a chemical reaction between $CaCO_3$ and aqueous phosphoric acid ($H_3PO_4$) to form a calcium phosphate solution. The precipitation process occurs when a KOH solution is added to a Calcium Phosphate solution until it reaches an acidity level in the pH range of 3 to 11. The sintering temperature in the range of 400 – 700℃. At a pH of 10 and a calcination temperature of 600℃, the product composition was obtained with calcium oxide (CaO) of 44.60%, potassium oxide ($K_2O$) of 6.65% and phosphorus ($P_2O_5$) of 38.58%.

**Keyword** : calcium carbonate, fertilizer, potassium hidroksida and precipitation

***Abstrak***

*Kalsium karbonat ($CaCO_3$) merupakan material yang banyak terdapat di Indonesia, baik dalam bentuk batuan maupun dalam berbagai jenis limbah cangkang kerang. Penelitian ini memanfaatkan batuan $CaCO_3$ sebagai sumber CaO untuk pembuatan komposit kalsium-kalium-fosfat (Ca-K-P) dengan metode presipitasi. Komposit Ca-K-P dapat digunakan untuk memperbaiki kualitas tanah masam, perakaran dan kualitas tanaman karena adanya unsur kalsium (Ca), kalium (K) dan fosfor (P). Unsur fosfor merupakan hasil reaksi kimia antara $CaCO_3$ dengan asam fosfat encer ($H_3PO_4$) membentuk larutan kalsium fosfat. Proses presipitasi terjadi ketika larutan KOH ditambahkan ke dalam larutan Kalsium Fosfat hingga mencapai tingkat keasaman pada kisaran pH 3 – 11. Suhu sintering pada kisaran 400 – 700℃. Pada pH 10 dan suhu kalsinasi 600℃, diperoleh komposisi produk berupa kalsium oksida (CaO) sebesar 44,60%, kalium oksida ($K_2O$) sebesar 6,65% dan fosfor ($P_2O_5$) sebesar 38,58%.*

***Kata kunci** : kalsium karbonat, pupuk, kalium hidroksida dan presipitasi*

## INTRODUCTION

Calcium carbonate is known to have been widely developed as a basic material for quite extensive applications, including for the formation of functional materials in the fields of medicine (Habraken et al. 2016; Zaman et al. 2020), health (Thomas et al. 2015), and the material industry. Precipitated calcium carbonate (PCC) can be obtained from various shells with varying polymorphs (Buasri et al. 2013; Muljani, Saputra, and Sumada 2021). In previous studies, the formation of composites involving potassium elements have been reported using both the precipitation method (Muljani et al. 2018; Sumada, Muljani, and Pujiastuti 2019) and the calcination method (Muljani, Wahyudi, and Sumada 2016). $P_2O_5$-CaO-$K_2O$ compositions were synthesized using the melt-quench procedure (Alaoui et al. 2021). Calcium phosphate-based bioactive quaternary $P_2O_5$–CaO–$Na_2O$–$K_2O$ are used for biomedical applications such as dental, orthopedic, and maxillofacial (Marikani et al. 2008). Utilization of calcium carbonate rock, as a source of calcium for the formation of calcium-potassium-phosphate composites (Ca -K-P). This composite contains calcium (Ca), potassium (K) and phosphorus (P) elements which can be used to improve the quality of acidic land, improve the quality of fruits and plants in the agricultural sector and also be used for other needs.

The combination of calcium and phosphorus in nutrient degradation is needed considering that liming can release some phosphorus from the soil. On the other hand, in acidic conditions, calcium and phosphorus elements will become controllers. The synthesis of calcium-potassium-phosphorus composites (Ca-K-P) refers to the synthesis of calcium phosphate (Hussain 2019), namely by reacting calcium carbonate ($CaCO_3$) or calcium oxide (CaO) with phosphoric acid solution ($H_3PO_4$) and the precipitation process (precipitate formation) is carried out by adding a base solution. In the synthesis of calcium phosphate, the base solutions commonly used are sodium hydroxide solution (Al-Sanabani, Madfa, and Al-Sanabani 2013; Rincón Joya et al. 2016) and ammonium hydroxide ($NH_4OH$) (Komlev et al. 2010; Suzuki 2013). In the synthesis of calcium-potassium-phosphorus (Ca-K-P) composites, the solution used as a material in the precipitation process is potassium hydroxide (KOH). The chemical reaction that occurs in the synthesis of calcium-potassium-phosphorus composites (Ca-K-P) occurs through two stages of chemical reactions as follows:

$$CaCO_{3(s)} + H_3PO_{4(l)} \rightarrow CaHPO_{4(l)} + H_2O_{(l)} + CO_{2(g)} \quad \text{(i)}$$

The second reaction is a precipitation reaction using sodium hydroxide (NaOH) or potassium hydroxide (KOH) solution:

$$CaHPO_{4(l)} + H_2O_{(l)} + NaOH_{(l)} \rightarrow CaNaPO_{4(s)} + 2\,H_2O_{(l)} \quad \text{(ii)}$$

$$CaHPO_{4(l)} + H_2O_{(l)} + KOH_{(l)} \rightarrow CaKPO_{4(s)} + 2\,H_2O_{(l)} \quad \text{(iii)}$$

In the precipitation process, KOH was used because it will utilize K ions for soil fertilization applications. The pre-cipitation process generally occurs at pH 5 to pH 9. The degree of acidity (pH) in the precipitation process, the precipitation process occurs due to the addition of a base solution, in the production of calcium phosphate composites the precipitation process occurs at pH 5 - 7, the higher of the pH, the greater of calcium phosphate content that are deposited and at a certain pH it will be constant because there are no more solids that are deposited. In the production of calcium phosphate composites, the sintering temperature will affect the Ca/P ratio in composite products. Generally, the sintering temperature ranges from 500 – 900ºC. The higher the sintering temperature, the greater the Ca/P ratio, and at certain temperature conditions it will remain constant.

This study observed the effect of the acidity level (pH) on the precipitation process and the effect of sintering temperature on the composition and characteristics of calcium-potassium-phosphorus (Ca-K-P). Scanning Electron Microscopy (SEM) were used to analyze the effect of sintering temperature to morphology properties of product obtained.

## MATERIALS AND METHODS

$CaCO_3$ rock has a CaO content of 98.65%, with $Fe_2O_3$ impurities of 0.635%. Phosphoric acid ($H_3PO_4$) 10N and potassium hydroxide (KOH) 7N were obtained from a chemical store. $CaCO_3$ was ground to a size of 100 mesh. Reacting 25 g of calcium carbonate with 10 N phosphoric acid solution, a filtration process was carried out to separate the insoluble calcium carbonate from the filtrate. The resulting filtrate was subjected to a precipitation process (formation of sediment) by adding 7N potassium hydroxide, the addition of potassium hydroxide was carried out until the filtrate produced solids, namely at pH 4, 6, 8, 10, and 12, the solids obtained were filtered and washed until the pH was neutral, then dried at temperatures of 100, 125, 150, 175, 200 and 225°C, which called sintering temperature. The resulting product was subjected to composition analysis using the XRF method to determine the levels of calcium oxide (CaO), phosphorus ($P_2O_5$) and potassium oxide ($K_2O$). The experimental procedure is as presented in the flow diagram in Figure 1.

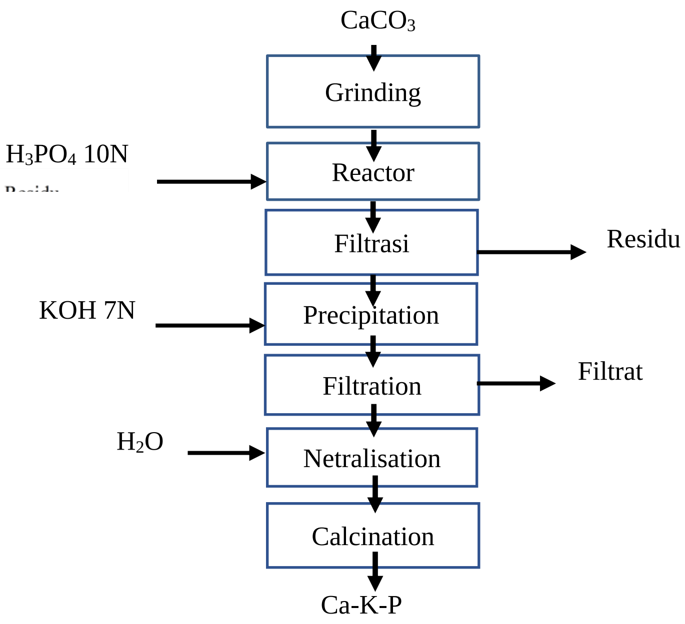
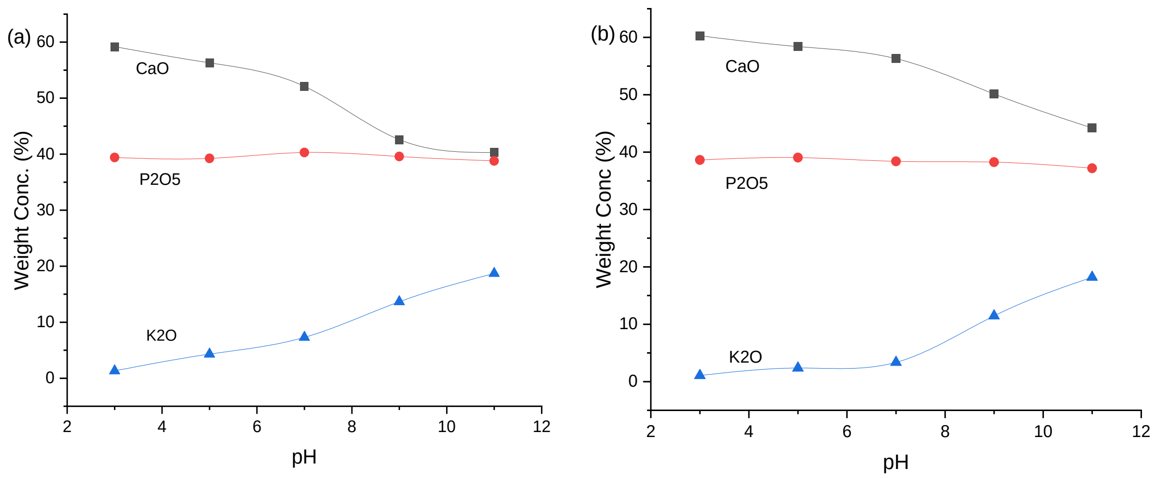



**Figure 1**. Flow diagram of the experiment on the formation of Ca-K-P composite from $CaCO_3$

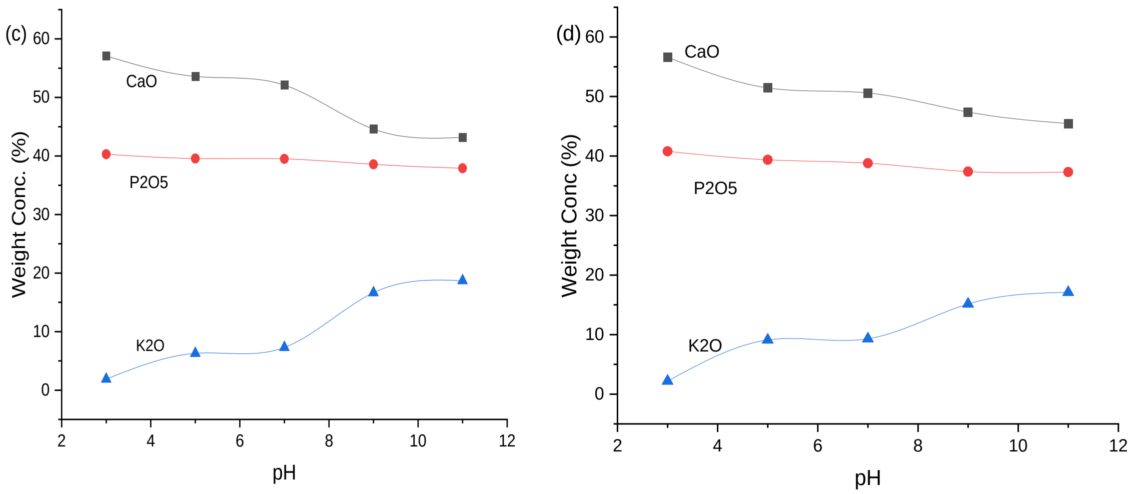
## RESULT AND DISCUSSION

### Effects on pH to Ca:K:P Composition

In this study, the precipitation properties for subtances were investigated by a different level of pH. Moreover, the effect of pH to Ca:P:K composition are depicted in Figure 2. Out of all graphs in Figure 2 are shown that the highest CaO precipitated resulted at temperature of 500°C and at pH 3. Furthermore, the CaO is confirmed to precipitated much more readily in acidic conditions than alkali conditions, their weight concentration decreased as the pH increased. In the case of $K_2O$, precipitated of $K_2O$ weighted more at alkali conditions. The weight concentration of $K_2O$ increased as the pH escalated. The precipitated of $P_2OH$ stable at any pH conditions. However, Anomaly shows on Ca:P:K composition at 400 degrees. At pH= 7. The concetration at pH=7 of $P_2O_5$ at 500, 600, and 700 °C are always decreasing. But at 400°C the concentration is higher than the other temperature.




(a) (b)




(c) (d)

**Figure 2**. Effect of pH on Ca, P and K composition at temperatures a) 400°C b) 500°C c) 600°C and d) 700°C

## Effect of pH and Temperature on Calcium Oxide (CaO) Levels *in Composites*

Figure 3 illustrates the relationship between pH and sintering temperature on the CaO content in the composite. The concentration of CaO in the composite drops as the acidity level (pH) increases during the precipitation process. The reduction in CaO is attributed to its substitution by $K_2O$ during the precipitation process. The process results in the formation of a calcium phosphate bond ($CaHPO_4$), which then transforms into $K_2HPO_4$ or $CaKPO_4$ by either the replacement of H ion with K ion or the entry of K ion to replace H ion, respectively.

## Relationship between precipitation pH and phosphorus ($P_2O_5$) content

Figure 4 illustrates the impact of pH on the $P_2O_5$ concentration in the composite. The phosphorus concentration exhibited a minor drop as the pH increased, and it remained rather steady in comparison to the variations observed in the potassium and calcium composition inside the composite. CaO was substituted for $K_2O$ in the precipitation process to create a $CaKPO_4$ chemical bond. The drop in phosphorus content was not caused by the liberation of phosphorus ions from the $CaHPO_4$ bond, but rather by the infiltration of K ions, resulting in a modification of the fraction.

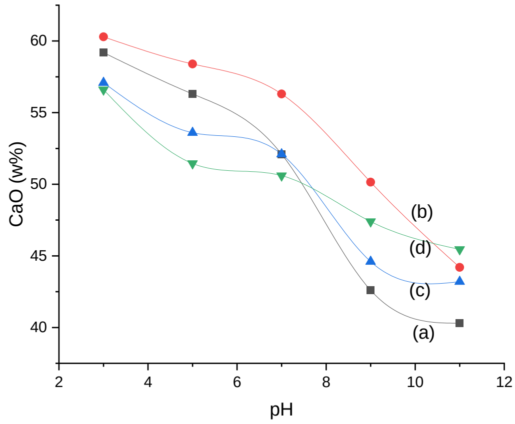



**Figure 3**. Correlation between precipitation pH and CaO concentration at temperatures a) 400°C b) 500°C c) 600°C and d) 700°C

Correlation between precipitation pH and $K_2O$ content is depicted in Figure 5. Concentration of $K_2O$ increases with increasing acidity levels (pH). The greater of potassium hydroxide volume, the higher of the precipitation pH. It can be evidenced that the process made the more potassium entered the $CaHPO_4$ bond and produced $CaKPO_4$. The results showed that the product contained CaO, $K_2O$, and $P_2O$ of 40-60%, 1-18% and 35-40% respectively.

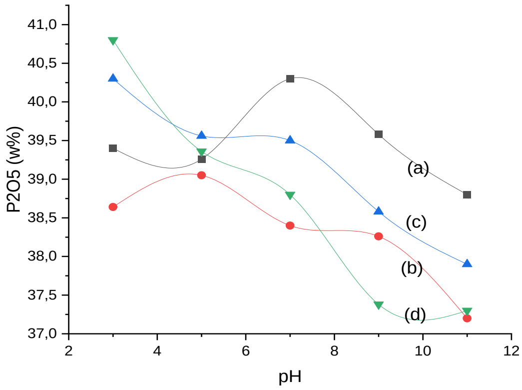



**Figure 4**. Relationship between precipitation pH and phosphorus ($P_2O_5$) content

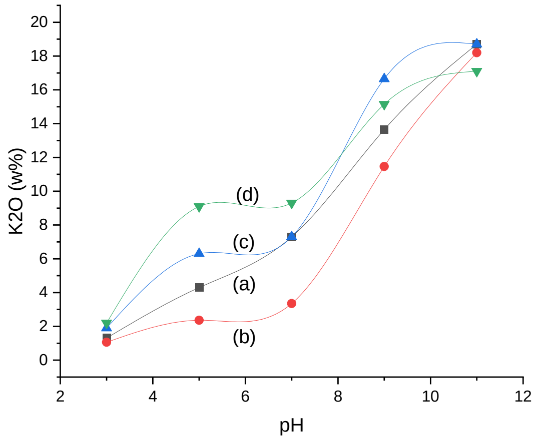
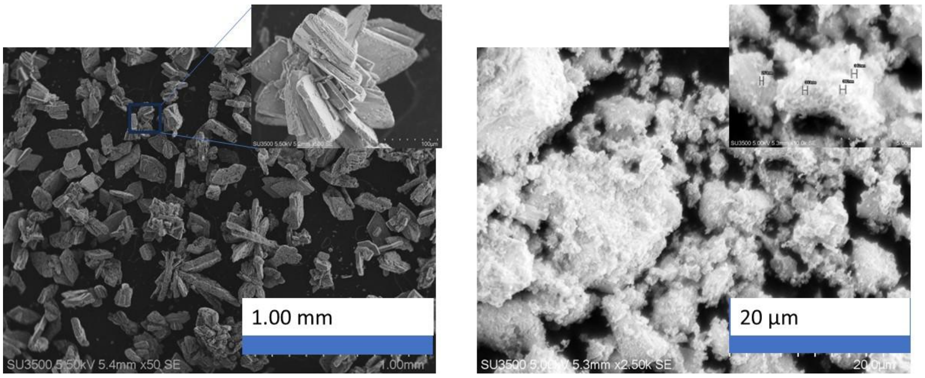



**Figure 5**. Correlation between precipitation pH and $K_2O$ levels




(a) (b)

**Figure 6**. SEM Image of $CaO$-$K_2O$-$P_2O_5$ composite at sintering temperature of a) 400°C and b) 700°C.

**Morphology of Ca-K-P**

The sematic image of morphology displayed via SEM is presented in Figure 6. It has been described previously that the composition of Ca, P and K has little effect on the sintering temperature, but morphologically, increasing the temperature from 400°C to 700°C can change the composite structure quite significantly, especially in the size and shape of the particles. Increasing the sintering temperature can reduce the size of the $CaO$-$K_2O$-$P_2O_5$ particles. The similar observation also reported, as the temperature increases, the size of calcium-phosphorus decreases. When the temperature is high, the solution of $Ca^{2+}$ ion transfer resistance decrease, the crystallinity and the grain size decline. As the sintering temperature rises, concentration polarisation reduces and ion transfer resistance falls, promoting the production of small dense grains (Yuan et al. 2023).

## CONCLUSION

The calcination temperature from 400ºC to 700ºC have a slight effect on the chemical composition of the Ca-K-P composite product, while SEM result showed a significant morphological changes. The precipitation process using potassium hydroxide (KOH) solution has a notable influence on the chemical composition of the calcium potassium phosphorus (Ca-K-P) composite obtained, especially the potassium oxide ($K_2O$) content. The chemical composition of the resulting composite fertilizer product was $CaO$ of 40-60%, potassium oxide $K_2O$ of 1-18% and $P_2O_5$ of 35-40%.

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