

# Reduction of $P_2O_5$ and F from Phosphogypsum by CaO addition

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**Abstract.** Waste of Phosphoric acid industry, which called phosphogypsum consists of 65% gypsum, 25% water and 10% impurities. Phosphogypsum can only be used up to 15% and the rest is thrown away. The objective purpose of this study is to reduce the content of  $P_2O_5$  and F using best variable CaO and stirring during coagulation process, flocculation and sedimentation. The method of this experiment is conducted by using the ratio of phosphogypsum and variable distilled water 1:1, 1:2 and 1:3, and then put it into a jar test using the variable stirring of 100 and 150 rpm. Then 11, 12 and 13 gram CaO and 50 ml distilled water is added as variables for coagulation – flocculation process. pH is kept at 6 by adding 4% NaOH. Polyaluminium chloride (PAC) 0.1% as much as 1.75 mg/l is added into the mixture and stirred at 30 rpm for 20 minutes. The separation of  $P_2O_5$  and F, is done by the sedimentation process. These experimental results show that variable 1:2 (w/v), 12 gram CaO and 150 rpm stirring able to reduce fluoride and  $P_2O_5$  up to 98.5% and 50% from phosphogypsum.

## 1 Background

Phosphogypsum (PG) is a byproduct of industrial phosphoric acid and gypsum consists of 65-70% gypsum, 25-30% water and 5-10% water impurities, ie phosphoric acid and its salts, hydrofluoric acid and its compounds,  $R_2O_3$  ( $Al_2O_3 + Fe_2O_3$ ), Quartz, apatite, alkali, organic matter, and others. Some of dirt as  $P_2O_5$  and F can be found in three different forms, namely in the gypsum crystal surface as water-soluble compounds ( $H_3PO_4$ ,  $Ca (H_2PO_4)_2 \cdot H_2O$ ,  $H_2SiF_6$ ), gypsum crystal lattice (solid solution  $CaHPO_4 \cdot 2H_2O$ ,  $SrSO_4$  or  $Na_2SiF_6$ ) and insoluble compounds, namely apatite and quartz (Al-Hwaiti, 2015).

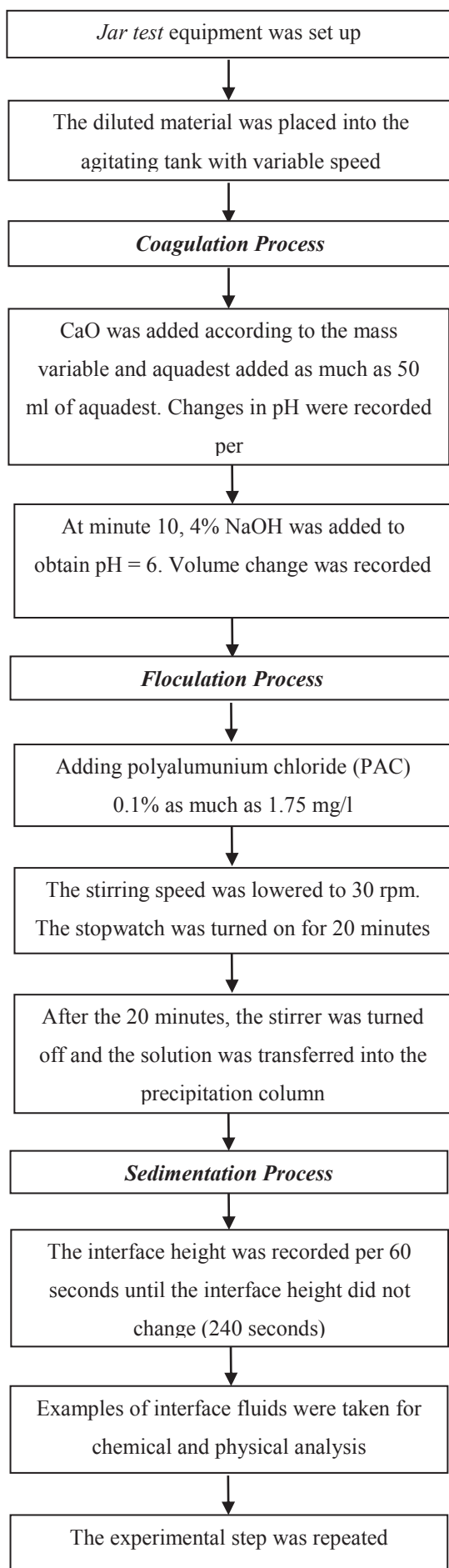
Only 15% of production worldwide is recycled, while 85% is stored around the factory in coastal areas. PG storage without prior processing can cause serious contamination of soil, water and atmospheric environments (Tayibi, 2008). In further treatment, phosphogypsum can be used for industrial purposes and infrastructure needs, one of which is cement. If used in the manufacture of cement, such impurities can disrupt mechanical properties by altering the gypsum morphology that will harden. Various methods have been suggested to reduce the reactivity of the impurities., including washing simple with water or filter wash solution from phosphogypsum the heating hemihydrate anhydrite followed by washing or neutralization with  $Ca(OH)_2$  or the base material, and treating phosphogypsum with a mixture of Sulfuric acid and silica or hot ammonium sulfate solution (Singh, 1992)

More pure PG without impurities will get more positive results for the environment and surrounding areas. So generally, this study aims to reduce the content of  $P_2O_5$  and F impurities especially in phosphogypsum by performing physical and chemical treatment and determine the effect of such treatment on the set parameters.

## 2 Methods

In this experiment, three main processes were coagulation, flocculation and sedimentation. In this experiment used a jar test tool to assist the process of blending in the process of coagulation and flocculation. While the process of sedimentation used measuring glass 1 liter to know the best sedimentation process. The process is seen in the picture below

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### 3 Result

#### 3.1 The Effect of Dilution Variables, CaO Mass, and Stirring Rate on Change in pH

In this experiment the pH measurement aims to determine the best pH performance during the coagulation process. The pH changes in the solution occurred every minute, and was measured for 10 minutes in 1: 1 (w / v), 1: 2 (w / v) and 1: 3 (w / v) dilution variables at 100 and 150 rpm, and CaO mass of 11, 12, and 13 gram, could be seen in Fig. 1 and 2. At a speed of 100 rpm, various pH changes occurred in the range of 12.6 to 13.6. This indicated that the phosphogypsum solution was in a high alkaline condition. In the ideal coagulation process the pH of the solution was in the range 7 to 8, which at pH 7 to 8 was the ideal pH for the occurrence of coagulation. However, in this experiment the solution pH was a base in the high pH range, resulting in deviations in the pH value achieved. In this case, it could be seen in the above three samples (Fig. 1) that the best performance of pH occurred at pH 12.6 in sample 2. While at a stirring speed of 150 rpm, the best performance of pH occurred at pH 13 in sample 4 (Fig. 2).

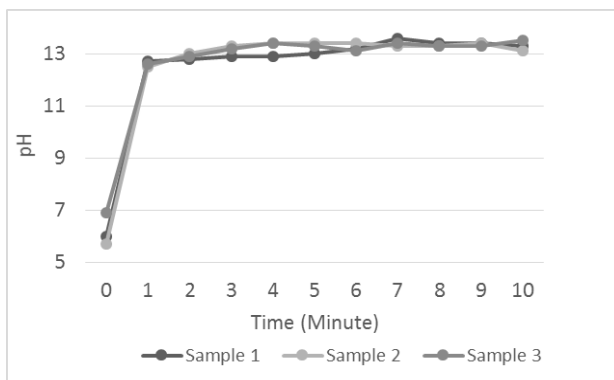


Fig. 1. Change of pH in solution to time at speed of 100 rpm with ratio 1: 1

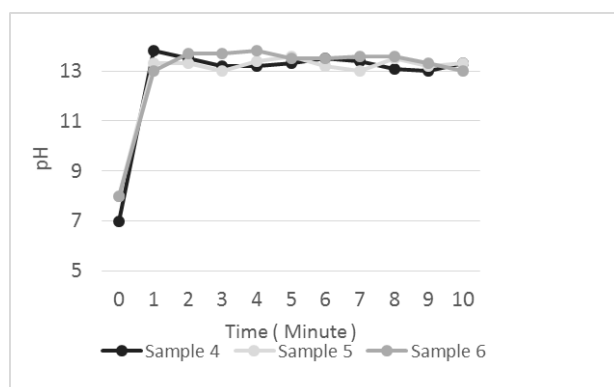
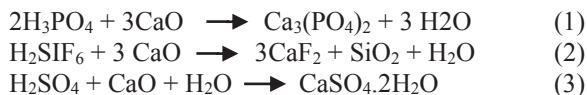


Fig. 2. Change of pH in solution to time at speed of 150 rpm with ratio 1: 1

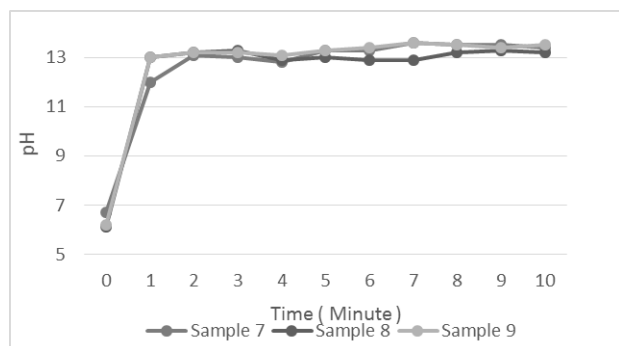
The best performance of the results was achieved at pH value of 12.5 with stirring speed of 150 rpm. This could be occurred because of the influence of several factors that affect the coagulation and flocculation process, such as pH. Coagulation was an important process in this experiment, because coagulant serves to bind impurities (P<sub>2</sub>O<sub>5</sub> and F) contained in the solution which will be deposited. The reactions were:



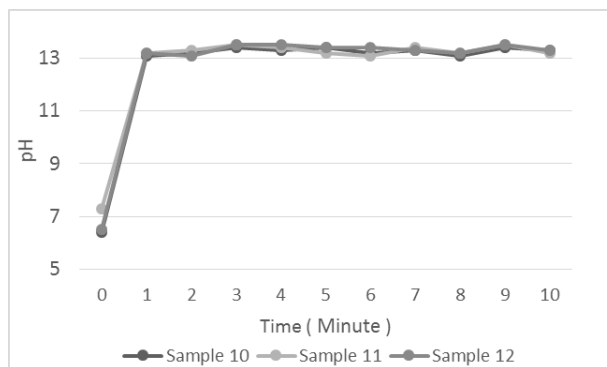
PH in each variable indicated fairly high base condition, where the conditions achieved exceed the optimum pH at coagulation and flocculation ie pH 7 to 8. This condition was achieved due to the effect of adding CaO as a coagulant in the coagulation process, in which CaO can increase the alkalinity of the solution with an initial pH of 5 to 6. However, the conditions achieved did not meet the optimum conditions, because of the excessive amounts of CaO as coagulants, causing a rise in pH under fairly high base conditions.

Furthermore, on the dilution variables of 1: 2 (w/v) at a rate of 100 rpm and 150 rpm, and the CaO of 11, 12, and 13 gram mass variables were also measured pH on each sample performed every minute for 10 min.

For a speed of 100 rpm in this variable, the pH range occurring, was still in a high alkaline pH condition with a pH value of 12 to 13.6. The best pH performance in this experiment can be achieved, although the ideal pH range occurring in the coagulation process was 7 to 8. The best pH performance at 100 rpm stirring rate, showing the pH value of 12 in sample 7 (Fig. 3), compared with the other sample that have a higher pH value. As for the stirring speed of 150 rpm, the best pH performance occurred in sample 10 with a pH value of 13 (Fig. 4). The pH value in each sample, still under high alkaline conditions, was the same as the 1: 1 (w/v) dilution variables.



**Fig. 3.** Change of pH in solution to time at speed of 100 rpm with ratio 1: 2

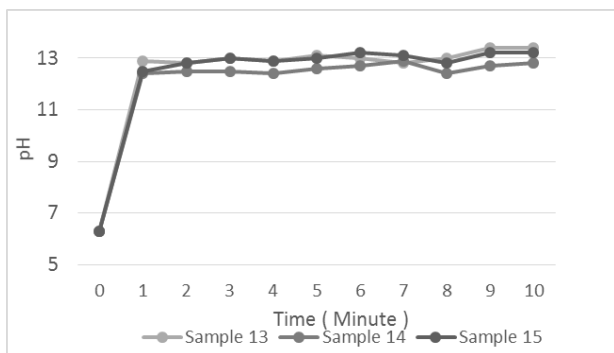


**Fig. 4.** Change of pH in solution to time at speed of 150 rpm with ratio 1: 2

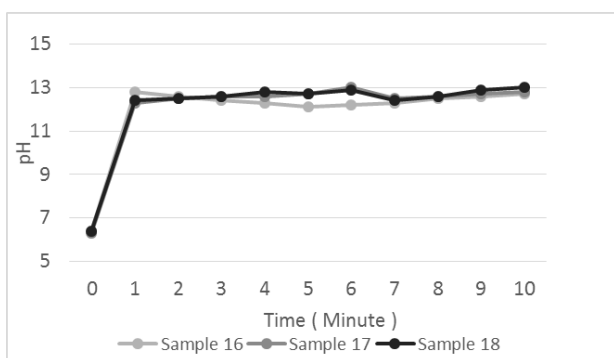
From the above variables, resulted the best pH performance at pH value 12 that occurred in sample 7. pH became one of the factors affecting coagulation process that occurred in this experiment. Coagulation was a process of destabilizing particles causing the joining of positive and negative ions to form a flock that was easily precipitated, so the coagulation process will also help the sedimentation process. In this case, the pH conditions achieved did not meet the ideal conditions of pH in the coagulation process due to excessive amount of CaO, but at the time of rapid agitation and the addition of CaO, 2 layers of solution indicated that the coagulation process occurred well. Coagulation served to bind the content of P<sub>2</sub>O<sub>5</sub> and F in the solution to be easy to precipitate in the sedimentation process. P<sub>2</sub>O<sub>5</sub> and F will be bound by the coagulant CaO as Ca<sub>3</sub>PO<sub>4</sub> and CaF<sub>2</sub> as salts at the precipitate formed.

In the dilution variables were 1: 3 (w / v) at 100 and 150 rpm, with CaO of 11, 12, and 13 grams, pH was measured every minute at 10 min.

For the speed of 100 rpm resulted the pH value of each sample under high alkaline conditions. In this experiment, there was a pH drift in the coagulation process, where the ideal pH in the coagulation process was 7 to 8. The pH conditions achieved in this experiment were high bases, so in this experiment the best pH performance of this variable was obtained in sample 15 with pH 12.3 (Fig. 5), whereas at a speed of 150 rpm showed the best performance resulted at pH12.1 in sample 17 (Fig. 6). Coagulation was performed on this process using rapid stirring aid, and CaO as coagulant. Aside from being a coagulant, CaO also serves to increase the alkalinity of the starting solution having an initial pH of 5 to 6. Addition of the amount of CaO performed in this experiment was excessive, thus causing an increase in pH value under basic conditions. Although within the pH range of coagulation, the pH achieved was not in ideal conditions, but the coagulation process could occur from the formation of 2 layers during stirring.



**Fig. 5.** Change of pH in solution to time at speed of 100 rpm with ratio 1: 3



**Fig. 6.** Change of pH in solution to time at speed of 150 rpm with ratio 1: 3

The suspension formed from this experimental process had properties of electrical properties, which inhibited agglomeration of particles and sedimentation, and the stability of the suspension was caused by the electrostatic forces contained in the suspension. In various industrial waste suspensions, most suspensions had negative ions. So to reduce the electrostatic force of particles it was necessary to neutralize the particles, so that the coagulation process, flocculation, and sedimentation could occur well. With the addition of coagulant, the electro-plastic force became low, and the suspension became unstable due to the presence of positive ions in the coagulant, thus causing the particles binded to form flocks and also affected by rapid stirring aid. In this process also used auxiliary coagulant that was PAC (Poly Aluminium Chloride) which helped to enlarge flock which had happened at previous process, which would collide because of particle agglomeration and felt down because particle weight became heavier. In addition PAC also served to help control the electrostatic force on the suspension. PAC was a heavier molecular weight polyelectrolyte and contained adsorbers which served as flocculant intermediate flock [6].

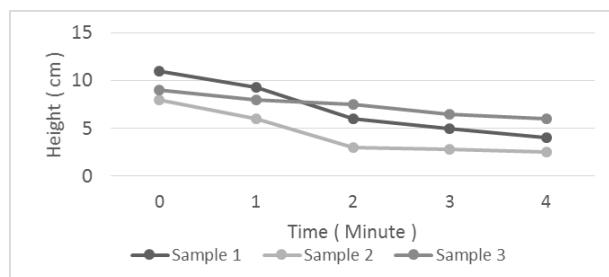
For pH parameters achieved did not meet the optimum conditions of coagulation and flocculation process, but the coagulation and flocculation process occurred well with the formation of 4 layers in the

sedimentation process. This was because coagulant reactivity was high CaO. CaO was an alkaline earth metal which was a highly reactive group of IIA elements and can react with water. The reactivity of the alkali metal was closely related to the two valence electrons and the relatively large radius of the atom. As a result, alkali metal easily releases its valence electrons to form a charged cations (+2), and dissolves in water. Therefore CaO could bind impurities (P<sub>2</sub>O<sub>5</sub> and F) to easily deposited compounds in the coagulation process, and canceled the negative ion ions present in the suspension, binded each other with the positive ions of the coagulant, due to the high valence, so that the coagulation process proceeds well .

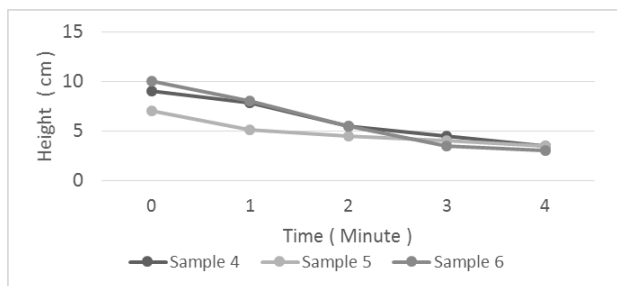
### 3.2 The Effect of Dilution Variables, CaO Mass, and Stirring Rate on Sedimentation Results

Changes in the sedimentation altitude of the solution per minute, measured for 4 min at 1: 1 (w / v) dilution variables at 100 and 150 rpm, and CaO of 11, 12, and 13 grams, could be seen in (Fig.7) and (Fig. 8)

At a stirring speed of 100 rpm there was altitude change for each sample in the altitude range of 9.1 to 3.8 cm. The height measured was the height of the sludge interface with the clean liquid that occurred during the sedimentation process. Sedimentation was the process of separating solid and liquid particles based on the force of gravity. The measured altitude changes showed the sedimentation process that occurred, if the rapid precipitation speed, then the altitude changes showed a significant decrease. From the sample that had been measured, the best result of the change in sample 1 which was the first minute to the second minute with the value of 9 cm to 6 cm (Fig.7) with slope 3 cm / minute. While at a speed of 150 rpm, the best altitude change was in sample 4, the first minute to the second minute, with a value of 8 cm to 5.5 cm (Fig. 8) with a slope of 2.5 cm / min.



**Fig. 7.** Change of sedimentation height to time at 100 rpm with ratio 1:1

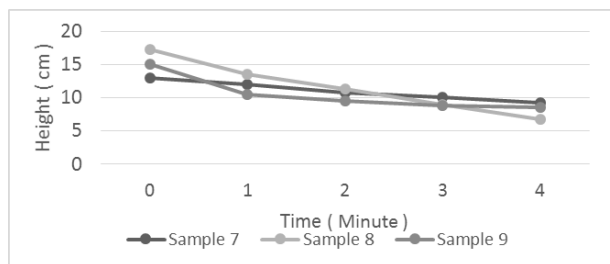


**Fig. 8.** Change of sedimentation height to time at 150 rpm with ratio 1:1

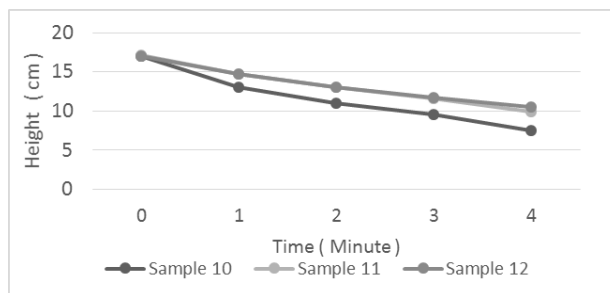
Sedimentation that occurred could not be separated from the influence of coagulation and flocculation processes that have occurred in the previous process. If the coagulation and flocculation process works well, then the sedimentation process would also work well. The coagulation and flocculation process was done with the help of coagulant ie CaO and PAC. In this process, binding of impurities and the formation of larger flocks occurs, so it was easy to precipitate. Later this process would help sedimentation of phosphogypsum solution, so that solid and liquid could be separated. The effectiveness of coagulant usage of CaO and PAC had significant effect. CaO had a high reactivity that helped the opposite ions to bind to form flocks, because of the high cation valency it was easy to release the valence. Although the parameters of pH conditions occurred in conditions not ideal, but with reactive CaO properties would help the sedimentation. While PAC was a very effective polyelectrolyte in this process, because the speed of the flock to be fast and produce good sedimentation. Thus the process runs well and forms 4 zones during the sedimentation process.

In the 1: 2 (w/v) dilution variables with CaO mass of 11, 12, and 13 grams, the stirring speed of 150 rpm made changes in altitude measured every minute for 4 min.

For stirring speed of 100 rpm and 150 rpm there was altitude changes during the sedimentation process took place. Sedimentation was done to separate solid and liquid particles based on the force of gravity. In the sedimentation process there was a change in altitude in the solution, the height measured was the height of the sludge interface with clear liquid. This process supported by a good deposition rate. If the speed of settling occurred rapidly then the sedimentation process that would work well, and marked by changes in altitude significantly. In this variable, the altitude changes of the best solution in the ninth sample at minute zero to the first minute, with the value of 14.9 cm to 10.1 cm (Fig. 9) with slope value of 4.8 cm/min. As for the speed 150 rpm, the best altitude change of the solution was in sample 10 at minute zero to the first minute, with the value 17 cm to 12.2 cm (Fig. 10) and slope value 4.8 cm/min.



**Fig. 9.** Change of sedimentation height to time at 100 rpm with ratio 1:2



**Fig. 10.** Change of sedimentation height to time at 150 rpm with ratio 1:2

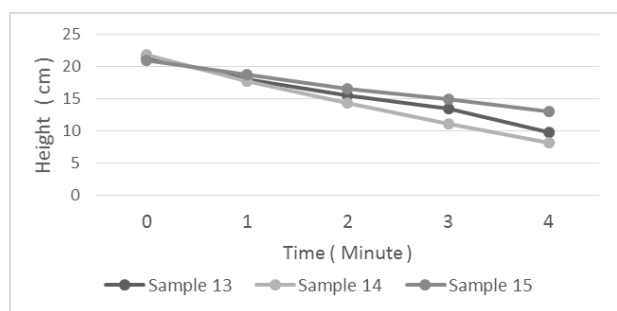
Sedimentation process was divided into four zones, namely liquid interface zone (layer 1), settling zone (layer 2), transition zone (layer 3), and compression zone (layer 4)

Before the sedimentation process occurred, the slurry was at the same concentration. During the beginning of the sedimentation process, sludge settled at the same rate. The settling rate was a function of the initial concentration of the particles in the solution prior to the sedimentation process. As a result of sedimentation, the precipitate deposits of this process reside in the compression zone located at the bottom layer of the settling process occurring at a constant rate. The transition zone would be occurred where the settling velocity decreases as a result of increased particle concentration. The solid concentration at the transition zone layer remains constant until the settling interface approaches the transition zone, and a transition zone was formed. Passing through this transition zone, the settling rate would decrease due to increased density and viscosity of the suspension surrounding the particles. If the layer rise of the sediment reached the interface, the compression zone would be formed. Sedimentation effects occurred due to several factors, such as the coagulation and flocculation process that had been formed previously which would help the process of sedimentation occurs. In the coagulation process that occurred using coagulant CaO, where the coagulant was very reactive and has the valence of cation (+2) which could easily release the ion to help neutralization, and the ion ion binding into a larger flock, so the role of coagulant was very influential to reach sedimentation conditions Which was good [6].

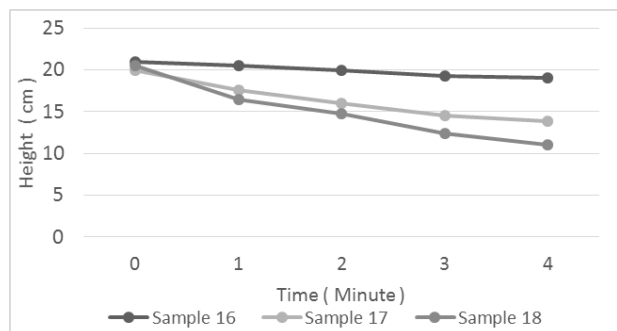
For 1: 3 (w / v) dilution variables with CaO mass of 11, 12, and 13 grams and stirring speeds of 100 and 150

rpm, measured changes in altitude of the measured solution per minute for 10 min.

In this variable, the sedimentation process that occurs could be seen in the Fig. 11. The measured altitude changes in each sample showed the sedimentation process took place. At such altitude changes, the settling rate affected the altitude changes. If the speed of settling worked quickly, then altitude changes showed significant value and the sedimentation process occurred well. Therefore, the best altitude change at 100 rpm was sample 13 from minute zero to the first minute with a value of 22 cm to 18 cm (Fig. 11) with slope value of 4 cm / min, while for 150 rpm the best altitude change occurred in sample 16 at minute zero to the first minute with a value of 20.1 cm to 16 cm (Fig. 12) with a slope value of 4.1 cm / min



**Fig. 11.** Change of sedimentation height to time at 100 rpm with ratio 1:3



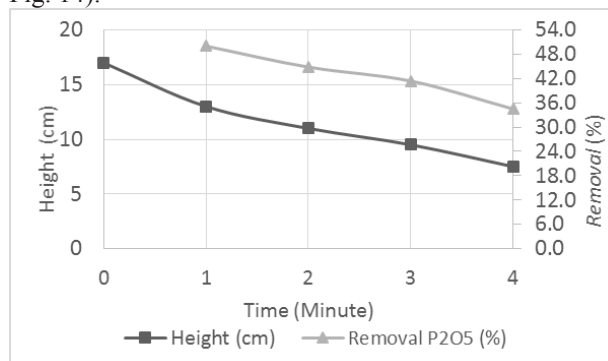
**Fig. 12.** Change of sedimentation height to time at 150 rpm with ratio 1:3

In the above explanation, it could be seen that there was a relationship that occurred in the process of coagulation, flocculation, and sedimentation. The use of coagulant was CaO and PAC could help the process of sedimentation was good. CaO had a very high reactivity and easily released its valence of +2, so it made it easy to bind negative ion ions, and made it a bigger flock. Easily ionic ions were bound, causing the mass density became larger which made the flock felt down due to the influence of gravity force, and finally settles. In addition, because the flock mass became larger, the density or the density of the flock became larger which made it easy to precipitate. With the ion ions merge into flocks, the concentration of the particles becomes larger and would slow down the settling speed. This results in the formation of a larger layer of liquid interfaces, as a result

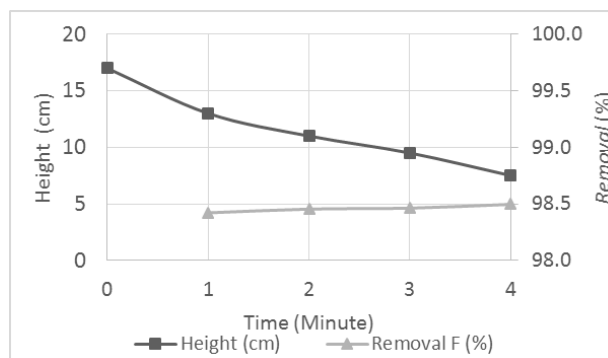
of the rising concentration of the solution and the felt of the flock downward, and the transition zone was formed. Deposition rate in this transition zone slows further due to the large particle concentration, and massive density. This condition would reach a stable state until the interface layer approached the sediment layer. When the layer rise of the sediment reached the interface, this was what drives the compression zone or compaction zone located at the bottom layer.

The forces that affect the sedimentation process were the drag force and impelling force. The force of impelling was the force caused by the gravity of particles or the force of gravity (downward), which caused the big flock to felt down. And buoyant force (buoyant, upward). While the drag force was a force against the impelling force so that the particles were in equilibrium. The direction of this style was upward. The particle mass caused a drag force and was balanced by the impelling force, resulted in a constant particle precipitation speed [6].

From 1 to 18 samples the best results were obtained on the 1: 2 (w / v) dilution variables, CaO of 12 gram mass, and 150 rpm velocity were analyzed to determine the concentrations of P<sub>2</sub>O<sub>5</sub> and F at layers 2 and 3, in the measured solution each minute for 4 minutes at the time of sedimentation. The % removal resulted of P<sub>2</sub>O<sub>5</sub> and F that had been analyzed at layers 2 and 3 during sedimentation could be seen in the picture with the relation of sedimentation and time height (Fig. 13 and Fig. 14).



**Fig. 13.** The relationship between height with% removal of P<sub>2</sub>O<sub>5</sub> over time



**Fig. 14.** The relationship between height with% removal of F over time

From the above two figures, different results were obtained on % removal of  $P_2O_5$  and F. The above results showed that the % removal F was greater than the % removal of  $P_2O_5$  (Fig. 15 and Fig. 16), there was a decrease of F concentration in layers 2 and 3, contains a lower concentration of F compared to other layers, whereas for  $P_2O_5$  concentrations, it had a greater concentration than other layers. In Fig. 16 the best % removal occurred in the first minute of 50% with a sedimentation height of 13 cm, and for the best % F removal occurred in the fourth minute of 98.5% with a height of 7.9 cm. In this case there was an anomaly in the removal results for  $P_2O_5$ , where there was a decrease in concentration in the first minute and the increase in concentration in the second minute to the fourth minute. This occurs because of the restabilization conditions in the coagulation and flocculation process, caused by the addition of excessive amounts of coagulants, resulting in poor coagulation and flocculation (ASWW, 1998).

This difference in yield could occur due to the effect of the flock size of  $P_2O_5$  and F, which had different sizes. The size of the flock affected the determination of the precipitation characteristics of the flock. In this case the particle diameter became an effect on the coagulation process, flocculation and sedimentation. So the particle diameter would determine the location of the particle concentration decrease, ie at the top layer or in the bottom layer of the sedimentation. In addition, other conditions affected the result difference were the effects of interactions between  $P_2O_5$  and F particles which had the same surface area loads produced on electrostatic forces that made them difficult to agglomerate and settle (ASWW, 1998).

In this case the interaction between the particles of  $P_2O_5$  has a larger load surface area than the particle F, so that the particle was difficult to achieve agglomeration and was difficult to precipitate, compared to the more agglomerated F particles and could be precipitated well during the sedimentation process. The result of F concentration decrease was greater than  $P_2O_5$  indicating that the coagulation, flocculation, and sedimentation process works well. Another factor was the size of the particles  $P_2O_5$  and F that affected the occurrence of particle agglomeration. In this case the particle diameter and deposition rate were directly proportional, so the larger the particle diameter the greater the precipitation speed occurs. If the settling speed was faster, the sedimentation process proceeds well, and flocks formed in the coagulation and flocculation process can be well deposited during the sedimentation process. Therefore, F particles more easily precipitate due to larger particle diameter size and better settling rate (ASWW, 1998).

The reactivity of the coagulant also affected the results of % removal of  $P_2O_5$  and F. In this case the coagulant used was CaO. CaO had a cationic valence (+2) and was a highly reactive alkaline earth metal with water, which readily released ions to neutralize particles and helped agglomerate the ion ions to bind. F particles had high reactivity and high electronegativity, so this condition could affect the bonding bonds that occurred between the flocks that were formed. As a result of higher F reactivity and electronegativity compared to

$P_2O_5$ , ionic ions would be easier to bind and neutralization processes. So in this case the F particles more easily binded to the CaO and form precipitates that were easily precipitated, the flock was bonded and the size becomes larger. F particles had water-soluble properties, where their solubility was high in water, which causes F particles to precipitate easily, compared with  $P_2O_5$  particles, hence F particles would more easily settle than  $P_2O_5$ . Thus, the above factor influences the difference in % removal yield between  $P_2O_5$  and F in the best samples, where the % removal occurred on particle F was greater than that of  $P_2O_5$  particles of 98.5%.

## Conclusions

1. Phosphogypsum can be used as a cement mixture because the  $P_2O_5$  and F content of the phosphogypsum has decreased, so that the phosphogypsum for the cement mixture can be drawn from layers 2 and 3 at the time of sedimentation.
2. The addition of CaO mass, stirring speed variables, and dilution variables affects the coagulation, flocculation, and sedimentation processes for the pH performance parameters that occur in each experimental sample and CaO reactivity as well as rapid stirring that affected the occurrence of layers during coagulation, flocculation, and sedimentation took place.
3. The percentage decrease of  $P_2O_5$  and F concentration occurs at the best condition (layers 2 and 3), with 1: 2 (w / v) dilution variables, CaO of 12 gram mass and stirring speed of 150 rpm. The result is to decrease  $P_2O_5$  concentration by 50%, and decrease F concentration by 98,5%.

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