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PRELIMINARY STUDY OF PARTICLE SIZE MEASUREMENT OF FINE PHOSPHATE ROCKS USING DYNAMIC LIGHT SCATTERING METHOD

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ABSTRACT

Particle size measurement is an important role in the utilization of phosphate rocks for nanofertilizer. In this study, the phosphate rocks from Wonosari and Ciamis were milled by planetary ball mill (PBM) into submicron size (0.19 µm). Measurements of the submicron size were conducted using a dynamic light scattering (DLS) method, i.e. iluminating. The milled products were also compared to the milled zeolite and bentonite from the same PBM. There is a relationship between the particle milled size and its chemical composition. The correlation is interpreted as the result of different hardness in minerals content.

Keywords: phosphate rock, particle size analyzer (PSA), dynamic light scattering (DLS), planetary ball mill (PBM)

INTRODUCTION

The use of nonmetallic mineral depends on its degree of processing, including the ultra-fine pulverizing, superfine grade, fine purification and surface modification, etc. Therefore, ultra-fine pulverizer technology to a certain extent on the nonmetallic mineral products decides on the rational development and utilization effects. Research and development of nonmetallic minerals industries have made enormous development, its processing technology continues to improve, in providing industry and related fields of high quality raw materials requirements. Ultrafine pulverizing and classification technology have been properly met the demands of the 10 ~ 1 µm size for various types of nonmetallic mineral powder raw materials, for agriculture, automotive, paper, rubber, plastics, machinery, ceramics, microelectronics, specialty coatings, aerospace, composite materials industries (www.nanogloss.com, 2011).

One of the particle size measurement methods is Dynamic Light Scattering (DLS) which is a widely used to measure the size of particles and molecules in colloidal solution. The principle is that light intensity fluctuations taking place at microsecond or millisecond scales are measured. Those fluctuations are a measure of the diffusion constant (Brownian motion) of the molecules and are related to the hydrodynamic radius of a molecule (Li, 2010). This method has an advantage that can measure particle size, fast and accurate.

Scientific community is extremely excited about properties of small scale matter. These physico-chemical and optoelectronic properties could have superior utilization. These unique properties can be exploited to revolutionize the agriculture and food industries with efficient and cheaper fertilizers, new tools for the molecular treatment of plant diseases, rapid disease detection, enhancing the ability of plants to absorb nutrients, and can improve our understanding of the biology of different crops. Thus many scientists have been researching on that area to obtain fine to nano size by two methods either grinding or assembling the material. In addition, learning its characteristics and application also become main attention.

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Some companies have been intentionally developing analytical instrumentation suitable for characterizising particle size distribution in such a complex liquid system, such as cement, ceramic. paints, emultion and many more. But of course for the customers should choose the suitable instrument to apply on the measured samples. Some methods have been developed to measure particle size, one of them is Coulter Counter method which was invented in 1950s (Graham, M.D, 2003). Coulter determined that electrical charge could be used to determine the size and number of microscopic particles in a solution (www.en.wikipedia.org/wiki/Coulter_counter, 2011). Based on that principle, Coulter Counter able to measure the particle size in range 1 µm to 120 µm diameter (www.beckmancoulter.com, 2011). Due to this limitation, many companies and scienties developed the methods which can measure up to nano-scale. The instrument to adopt Dynamic Light Scattering method seems to have best principle for measuring the ultrafine to fine particle since it is covering the range of 0.6 nm to 7 µm (Herbani, 2008). However, On the measurement of particle size by DLS, there are some weaknesses to be faced. This is due to, DLS does not visualise the particles individually but analyses, using a digital correlator of the time dependent scattering intensity fluctuations. These fluctuations are caused by interference effects arising from the relative Brownian movements of an ensemble of a large number of particles within a sample. Through analysis of the resultant exponential autocorrelation function, average particle size can be calculated. However, it can come out to limited information about the particle size distribution profile compared to other measurement methods such as Nanoparticle Tracking Analysis (NTA) (www.nanosight.com, 2011)

In this study, the characteristics of fine particles were measured by DLS method, with phosphate minerals as a case study. It is important step in the study of phosphate minerals in order to reduce the cost of production and its sustainability reserves for a longer period, by investigating the efficiency of small size particle as phosphatic fertilizers. In the course of preparation, it is propose to synthesize fine particles of phosphate to be used as fertilizer.

METHODOLOGY

The basic theory of particle size measurement using dynamic light scattering is that a laser beam of light passes through a colloidal dispersion, the particles or droplets scatter some of the light in all directions. When the particles are very small compared with the wavelength of the light, the intensity of the scattered light is uniform in all directions (Rayleigh scattering) otherwise for larger particles (above approximately 250nm diameter), the intensity is angle dependent (Mie scattering). To differ small and larger size particles are:

- For small size particles: the scattered light intensity is relatively weak and distributed homogenously by broad angular scattered light.
- For larger size particles: the scattered light intensity is strong indicated by narrow angular scatered light. (Figure 1)

To simplify the understanding of DLS mechanism:

- measure the speed of Brownian motion and correlate it with the particle size
- illuminate particle with laser and analyze its scattering fluctuation intensity
- size dependence of scattering intensity

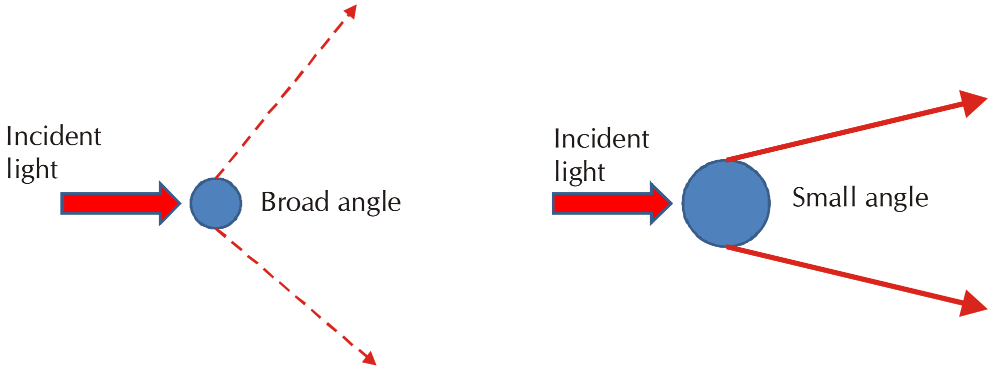


Figure 1. DLS mechanism at PSA (Herbani, 2008)

One of the advantage features in using PSA measurement is very compatible measurement for a small particle due to sharp peaks resulted and a very fast measurement, however for a larger particle, the measurement is slow and the broad peaks appeared. Figure 2 shows the tranformation process of light intensity that is catched by detectors to curves appearance.

EXPERIMENTAL

Materials

The phosphate samples were provided by Soil Research Centre, from Wonosari, Central Java (sample code: WS) and Ciamis, West Java (sample code: CM). The samples were dried at 105°C for 2 hours and then were crushed to -200 mesh using a jaw crusher and ring mill.

Procedure

The – 200 mesh phosphate samples were wet milled by PBM, at varied milling time of 10, 25 and 60 hours. During the milling, water was added to prevent the sticky particle to the jar wall and to lower aglomeration effect. (Suryanarayana, 2001). The next step, the particle size distribution of the samples were measured using Delsa Nano Particle Size Analyzer. During the measurement, water was added as a media. This measurement is based on DLS, which can be used to determine the size distribution profile of fine particles in suspension.

RESULTS AND DISCUSSION

Results of the milled samples using PBM are shown at Table 1. The best time for milling samples is 60 hours. It reaches the average size of 0.19 µm and the range distribution size is in between 0.08 - 0.25 µm. Particle Size Distribution of phosphate rocks plays an important role in understanding its physical and chemical properties. It affects the strength and load-bearing properties of rocks and soils. It also has an effect on the reactivity of solids participating in chemical reactions, and needs to be tightly controlled in many industrial products. In this case, if the phosphate rock is used as fertilizer then it should be correlated to enhance the ability of plants to absorb nutrients (P). Moreover, there would be no competition with silicic acid and also no fixation by calcium. (anonym, http://www.cazrj.res.in/naip/brochure.pdf). The lower, the size, the efficient the usage. Consequently, it will be lowering fertilizer cost.

Comparing the two samples (WS and CM), Wonosari phosphate is slighty easier to be milled than that of Ciamis phosphate. Milling result is more than 10 times. It is assumed that mineral composition of the phosphate rocks and its impu-

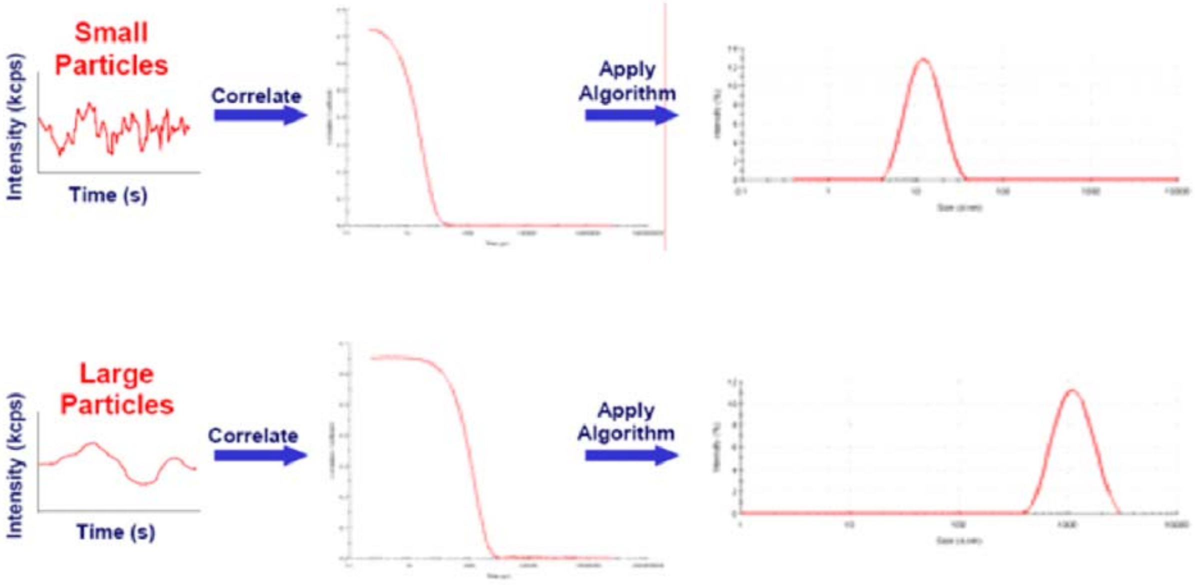


Figure 2. Tranformation process for data processing of DLS (Malvern, 2001)

Table 1. Milled phosphate rock samples from Wonosari and Ciamis using PBM

Milling Time (hours)	**Size (µm)**			
	WS		CM	
	Average	Range	Average	Range
10	0.34	0.28-1.49	3.22	2.87-3.82
25	1.28	0.99-5.59	17.27*	1.63-71.80
60	0.19	0.08-0.25	1.48	1.20-1.94

rities contribute to the hardness. In addition, measurement of 25-hour, milled Ciamis sample provides unsetisfied results.

Figure 3 shows the largest particle size of CM sample property (17.27 µm) when it was milled for 25 hours. The increase particle size may be caused by precipitation occured during the measurement that related to the time delay preparation after milling. A volume of the sample placed in the chamber would influence the determination. According to PSA standard procedure, the sample volume of the apparatus chamber must not be filled up more than 1 mL. Otherwise, fast precipitation would occur to disturb and lead to a wrong measurement. Another assumption is that milling time affects the aglomeration process. During 30-hour miling time, the small particles strongly aglomerate to have Van Der Walls bond, and it might be broken down at milling time of 50 hours. This phenomenon usually occurs due to a lot of metals content within the rocks. This fact corelates with high calcium content with phosphate rocks. This phenomenon can be shown at the measurement of WS 10H and CM 10H (Figure 4).

In Figure 4, the left side curve (WS 10H) appears as a half arch form, from the top. It decreases steeply. This phenomenon can be explained as follows: first it is dominated by the low particle size distribution of 0.28 micron; intensity of 30 %, then it is followed by higher particle sizes with lower intensity. This phenomenon explains the mechanism during miling process, that the large particle was scarped to produce smaller particle a lot and it took place continuously to the end of the process (Figure 5a). In addition, this mechanism resulted the rest with a few of bigger particle. On the other hand, the right side curve (CM 28) ap-

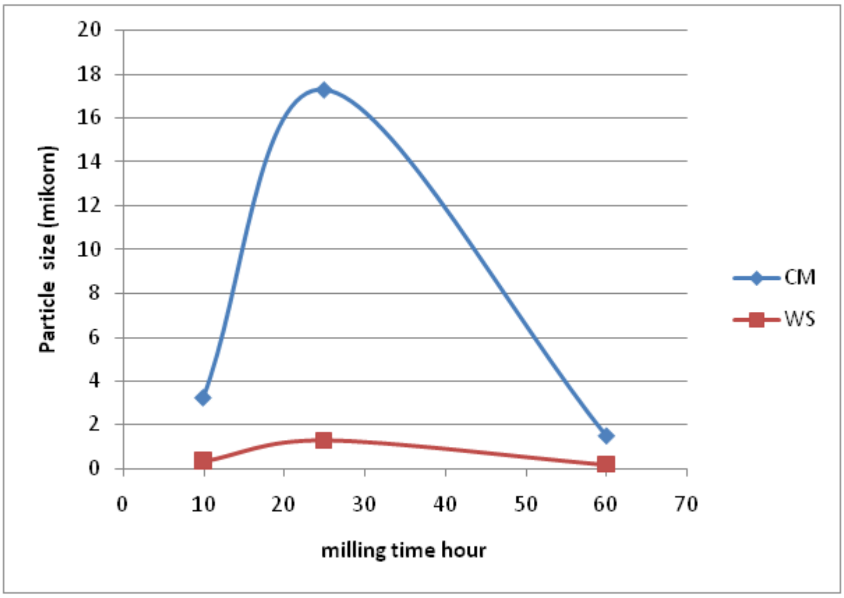


Figure 3. The particle sizes of Wonosari and Ciamis phosphate rocks, milled at 10, 25, 60 hours

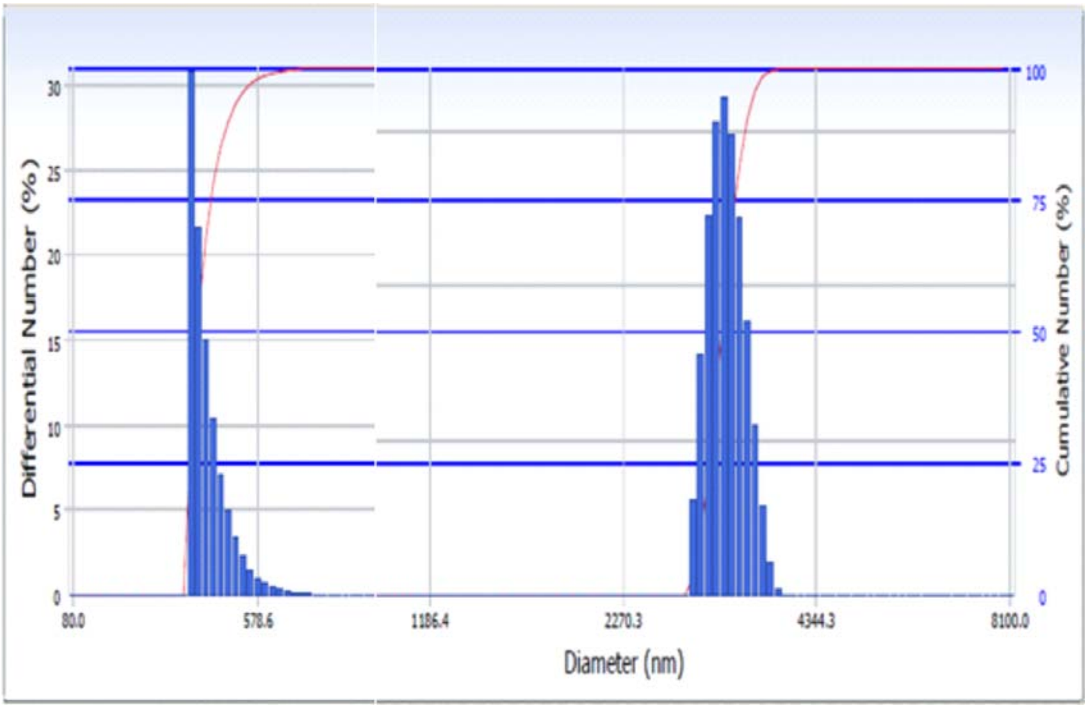


Figure 4. Number distribution curves of WS 10H (left side curve) and CM 10H (right side curve)

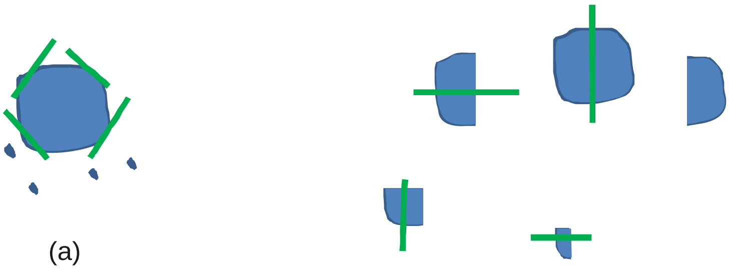
pears as arch form (bell form). It is started from 2.86 micron; intensity 3 %, which is rises up to 28 % for 3.18 micron then decreases to intensity of 0.2 % for 3.82 micron. This patern gives the understanding of the range of the particle size and the intensity of each particle size. Moreover, the curve is affected by the mechanism during milling process. The particle was splitted into two parts and the half part was devided into two parts. This occured continuously and fisnished after the milling process was stopped (Figure 5b). This mechanism produced a few of smaller particles, a lot of bigger particles and then a view bigger particles to form bell form. (personal communication).

Besides the volume, sample stability and homogeneity also have an important part in this measurement. Figure 6 shows the measurement of homogen and unhomogen samples.

Figure 6(a) shows one group curve that is started from around 1,000 to 3,000 nm. However Figure 6(b) shows 2 group curves. Those are around 1,500 and 70,000 nm. Consequently, in calculating the size, it obtained from the mean of the first and the last curves, which leads to the invalid determination. The peaks appear due to the unhomogen colloidal solution. This is the reason why particle size of CM 25 hours was very high anmely around 1.63 to 71.80 µm, as the average of these values. To strength the understanding of the phenomenon, Malvern (2001) represented those two peaks as shown in Figure 7. The first peak measured at 5 nm, and the second one at 50 nm. As a result, the mean of particle size measured is around 28 nm.

This leads to opinion that particle size masurement is asserted by its stability and homogeneity. This can be anticipated by measuring colloidal solution immediatly after preparation to prevent precipitation.

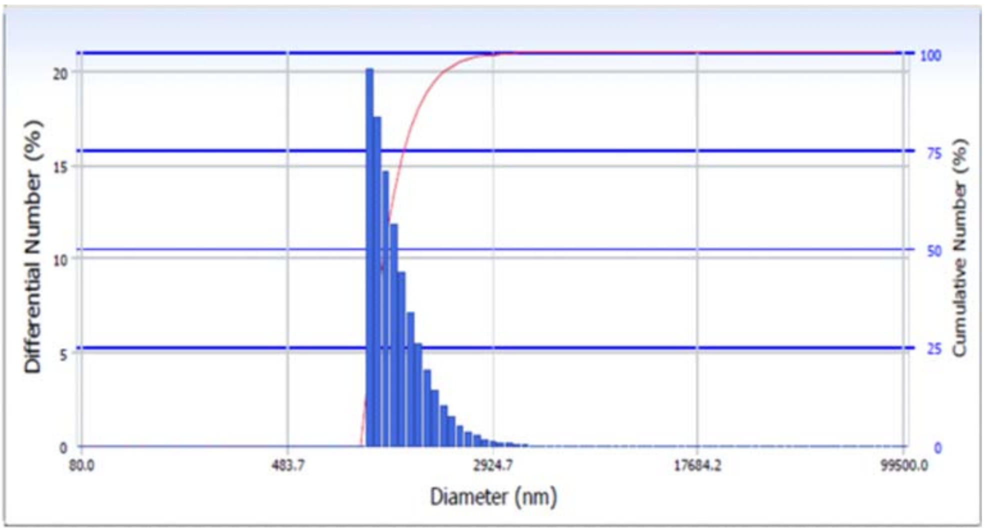
Recent work reported by Wahyudi et al. (2008) for Cijulang Ciamis' phosphate and by Wahyudi, et al (2010) for zeolite, and also by Wahyudi, et al (2010) for bentonite. Chemical compositions inform that phosphate rock, bentonite and zeolite contain SiO_2 16.71, 54.23 and 69.67 %, respectivelly. The silica content is subject to corelate to its high hardness compared to other minerals such as bentonite and apatite as the hardness of silica, bentonite and apatite are 7; 6-6.5; and 5 Mohs respectivelly. In addition, it is supported by the theory of chemical bonds amongs the minerals that hold atoms or ions together to form molecules. It is responsible directly for physical properties of the minerals including hardness.



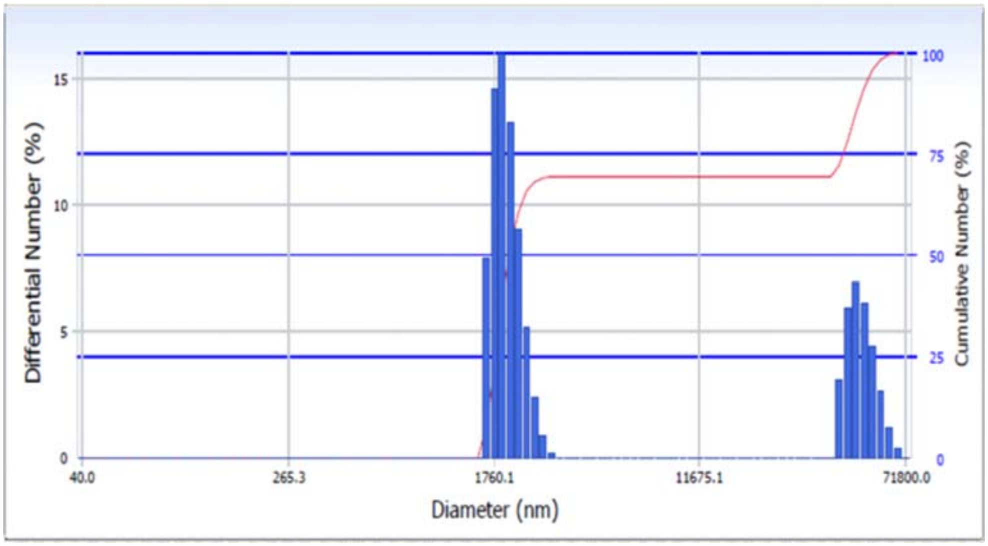
(a)

(b)

Figure 5. The miling mechanism of the two phosphate rocks



(a) Sample WS milled at 25 hours



(b) Sample CM milled at 25 hours

Figure 6. The differential of curves (a) stable and homogenous colloidal solution; (b) Unstable and unhomogenous colloidal solution

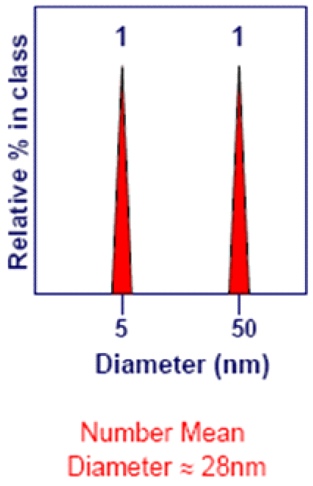


Figure 7. Ilustration of determined curves of particle size measurement to show two peaks (Malvern, 2001)

In general, stronger chemical bonds results in greater hardness. It seems that silica owns stronger chemical bonds than that of bentonite or apatite. However, it is found that the correlation between the silica content and the millled particle size at the same time period is not strongly clear (Table 2 and Figure 8), due to silica might be bound as its mineral's structures.

It is already believed that if aglomeration of ultrafine particle occurs, it will lead to the difficulty in reaching the nanosize. Effect of milling time shows three different paterns namely the paterns for zeolite, bentonite and phosphate rock. The lowest particle size for zeolite when it was milled for 10 hours, means that the aglomeration took place afterward. On the other hand, the aglomeration occurs after milled 30 hours for bentonite. For phosphate rock, it did not occur after, 60-hour milling. It is sug-

Table 2. Particle size of phosphate rock from Wonosari, and Ciamis, zeolite and bentonite.

Milling time	Phosphate Wonosari (nm)	Zeolite (nm)	Bentonite (nm)
10H	340	299.1	135.4
25H	1280	-	-
30H	-	344.6	77.4
60H	190	393	275.4

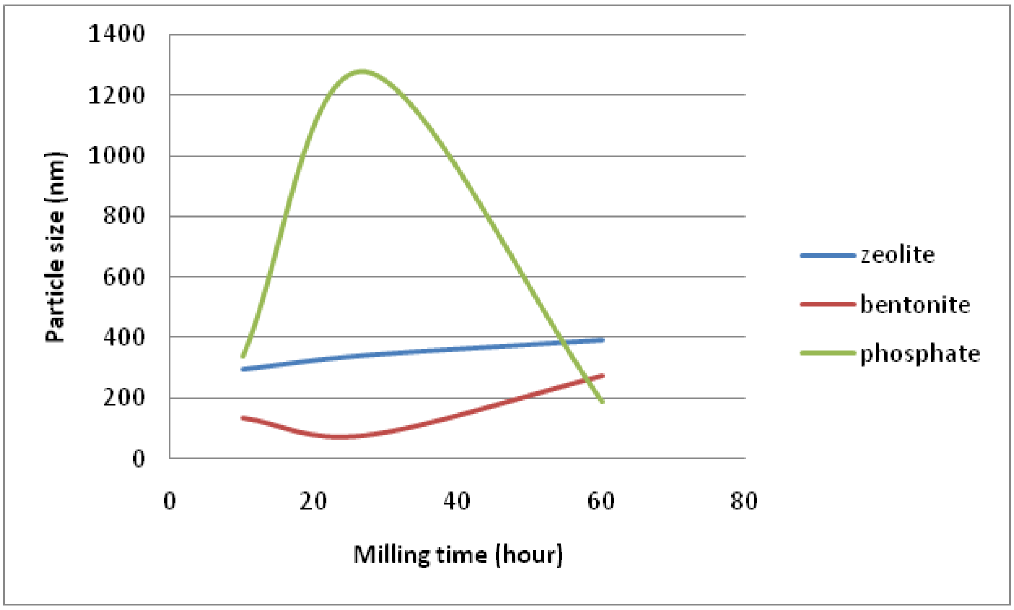


Figure 8. Particle size of phosphate rock of zeolite, bentonite and phosphate

gested that these paterns corelate to its mineral composition.

CONCLUSIONS

- The PSA can measure ultrafine particle by DLS method. For example the Ciamis's phosphate which can be measured until 190 nm, for 60-hour milling time.
- Homogen colloidal solution is the important factor to obtain valid result. Wrong result occur due to time delay during preparation. It cause precipitation process and an inaccuracy filling up the sample's volume during measurement.
- The DLS method informs a patern of particle sizes of the samples that correlates with the mechanism of milling process to result different curve types.
- Pulverizing mineral process to reach fine particle size is mainly affected by the hardness of mineral.

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