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MANUFACTURE OF GYPSUM BOARD FROM EGGSHELL WASTE MATERIAL

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ABSTRACT

Eggshell was waste from industrial and household that was found in much amount and really easy to found. Eggshell was contained $CaCO_3$ about 90 %w/w. CaO was main component of gypsum that could obtained from $CaCO_3$ processing, hence eggshell could be used as an alternative raw material for gypsum manufacture. $CaCO_3$ from eggshell could be used for gypsum manufacture by calcination process in the furnace at temperature 900 ^{0}C in order to deform $CaCO_3$ in the eggshell into CaO, then calcined material was mixed with aquadest and sulfuric acid solution and was stirred until precipitate was formed. Then, the precipitate must be filtered and dried in an oven until dried. The result was shown that increase the mixing concentration gave effect the increase of gypsum strength. The maximum result was shown in variation ratio of 35% calcined material, 50% aquadest and 15% sulfuric acid, with elapse time was 5.5 minute, load was 6.5430 lbs at compressive strength test. The composition of maximum result was shown 0.48% of SO_3, 7.68% of CaO and 0.98% of H_2O at XRD and SEM test.

Keywords: eggshell, gypsum, calcination, compressive strength, XRD, SEM.

INTRODUCTION

The rapid development in Indonesia, especially in the field of building construction make all stake holder, both public and private use of construction materials effectively. Since most of the construction materials were obtained by mining, for example, limestone mining, iron sand, and others. Given the amount of material from the mine will continue to decrease if exploited continuously and can cause negative impacts to the environment caused by mining activities. Natural gypsum mining in Indonesia alone, according to statistics from year to year the number increased as shown in Table-1 [1].

Table-1. Production, consumption, exports, imports of gypsum in Indonesia.

	Production (ton)	Consumption (ton)	Export (ton)	Import (ton)
Year 2003	2,287.961,81	1.643.760	16.289,57	660.491,38
Year 2002	2,350,787.95	1,578,709.11	51.55	772,130.39
Year 2001	406,500	1,442,459.25	36.38	1,036,124.34
Year 2000	810,000	1,353,925.50	1,012.36	546,721.23
Year 1999	542,000	1,137,278.84	3,540.81	507,790.03
Year 1998	555,500	1,046,440.34	373.33	582,126.56
Year 1997	2,110,000	2,623,857.22	-	513,603.56

Based on Table-1 in general the amount of gypsum production in Indonesia is increasing from year to year, although in 2001 had decreased but the next year continues to increase. Data on the number of consumption of gypsum in Indonesia looks fluctuating but generally increasing that began in 1997 with production 2,110,000.00 tons then the number decreased in 1998 and the next year increased to 2003. Data export of gypsum in Indonesia looks fluctuate from year to year, ranging from 1998 to increase until 2000 and then decreased in 2001 further increased to 2003. Gypsum import data in Indonesia is also seen to fluctuate from year to year starting from 1997 to increase until 1998 and then at 1999 has decreased then increased until 2001 and then decreased until 2003. Based on Table 1 also shows that consumption of gypsum in Indonesia is greater when compared with the production of gypsum itself. Both happened in the ratio of exports and imports of gypsum Indonesian amount is greater than the amount of exports and imports. This indicates the availability of gypsum for consumption in Indonesia is still less visible than the amount of production and import of high gypsum.

Towards support the increasingly rapid development will certainly use a lot of cement. Each year the number increased production of cement that can be seen in cement production data for each plant in Indonesia, as presented in Table-2 [2].

Table-2. Cement production data at factories in Indonesia.

Company name	Number of Cement Production in thousand tons a year					
	2010	2011	2012	2013	2014	2015
Pt. Semen Andalas Indonesia	1.600	1.600	1.600	1.600	3.200	3.200
Pt. Semen Padang	6.300	6.300	6.400	6.620	8.160	9.257
Pt. Semen Baturaja	1.250	1.200	1.350	1.600	2.600	2.700
Pt. Indocement Tunggal Perkasa, Tbk	18.600	21.100	21.100	21.100	20.100	23.100
Pt. Holcim Indonesia, Tbk	8.300	8.700	8.700	8.700	10.700	10.700
Pt. Semen Gresik, Tbk	9.100	9.724	11.300	13.120	13.120	13.120
Pt. Semen Tonasa	4.290	4.602	6.549	7.147	7.147	7.147
Pt. Semen Bosowa Maros	3.000	3.000	3.000	5.500	5.500	5.500
Pt. Semen Kupang	570	570	570	570	570	570
Total Annual Production	53.010	56.796	60.569	65.867	74.097	75.294

Of the Indonesian cement production data visible increase in the number of cement production continued to increase from the year 2010 until the year 2013 can even expect to continue to increase up to the year 2014 and 2015. To offset the increasing cement production will be required in the amount of gypsum that much anyway. As we know gypsum is a material blend of cement which makes cement can stick strongly. Therefore we need an alternative source of new manufacture of gypsum for example the manufacture of gypsum from waste eggshell.

Waste utilization was one right solution to solve the problems shortage of mine, for example, waste recycling eggshell into the manufacture of gypsum. This is in accordance with the Environmental Law No. 81 of 2012 regarding the management of household waste and household-like waste. Based on data from the egg production districts/cities of the Department of the provincial farm South Kalimantan years 2008 - 2011 as presented in Table-3.

Table-3. Egg production data regency/city of South Borneo.

No.	Years	Amount Of Production/Years (Kg/Years)
1	2008	15,431,286
2	2009	30,645,468
3	2010	28,990,293
4	2011	26,826,031

Based on the data of egg production in South Kalimantan visible amount of egg production in 2008 increased to 2009 and more than doubled and from 2009 to 2011 experienced a slight decrease in the number of egg production.

This study was conducted to make gypsum from waste eggshell. If this technology can be developed that will enhance the use value of eggshell waste, so that waste egg shells not only be waste from households, but can be used to something more economical.

GYPSUM

Gypsum is a white stone that is formed due to the deposition of sea water, then heated at 175 ° C which is often called by the name of stucco. Gypsum is one of the largest mineral in sedimentary environments is rock composed of minerals produced on a large scale are usually with persitipasi of saltwater. Gypsum is a natural insulator, warm to the touch compared to brick.

The chemical composition of gypsum material according to [3], i.e.:

1. Calcium (Ca): 23.28%
2. Hydrogen (H_2): 34%
3. Calcium Oxide (CaO): 32.57%
4. Water (H_2O): 20.93%
5. Sulfur (S): 18.62%

The Gypsum Physical properties according to [3], i.e.:

1. Color: white, yellow, gray, red, orange, black, if not pure
2. Specific gravity: 2.31 to 2.35 g / cm^3 / g / cm^3 water 25°C
3. Hard pearly especially surface.
4. Form minerals: crystalline, fibrous and massive.
5. Shine like silk
6. The low conductivity
7. System is monoclinic crystalline.

While the chemical properties of gypsum according to [3], i.e.:

1. Generally, containing SO_3 = 46.5%; CaO = 32.4%; H_2O = 20.9%
2. Solubility in water is 2.1 grams per liter at a temperature of 400 ^{o}C; 1,8gram per liter of water at 0 °C; 1.9 grams per liter at 70 – 900 ^{o}C.
3. Solubility increases with the addition of HCl or HNO_3.

Gypsum board is the generic name for a family of sheet products consisting of the main core of unburnt and coated with a paper on its surface. This is the terminology chosen for gypsum sheet products are designed to be used as wall, ceiling or ceiling and have the ability to be decorated. Strength gypsum board directly proportional to the thickness. Gypsum is formed under conditions of various purity and varying thickness. Gypsum is the first salt precipitates due to evaporation of sea water followed by anhydrite and halite, when salinity is growing. As evaporates minerals, gypsum precipitate shaped layer of sedimentary rocks of limestone, red shale, sandstone, clay,

and rock salt, and often shaped lens deposition in sedimentary rock units. Gypsum can be classified based on the place of [4].

According to data from the World Intellectual Property Organization (2009), in the United States, there are approximately 190,000 tons of waste egg shells, that of this amount, approximately 120,000 tons produced from the food processing industry and around 70,000 tons produced from hatching eggs. Meanwhile, in Indonesia the production of an egg shell will continue to abound for eggs produced in the field of animal husbandry and used in the restaurant, bakery and noodles as raw material for food. According to data from the Directorate General of Livestock [5], egg production in Central Java and Indonesia in 2013, amounting to 140 459 tons and 1,013,543 tons.

Dried eggshell contains about 95% calcium carbonate by weight of 5.5 grams [6]. Meanwhile, [7] reported that egg shell consists of 97% calcium carbonate. In addition, the average of eggshells containing 3% phosphorus and 3% consisting of magnesium, sodium, potassium, zinc, manganese, iron, and copper [6].

The word comes from the Latin calcination is calcinare which means burning lime. The most common calcination process is applied to the decomposition of calcium carbonate (limestone; $CaCO_3$) into calcium oxide (lime grilled; CaO) and carbon dioxide (CO_2). Product of calcination is usually called "calcine", which is a mineral that has undergone a process of heating. Calcination process is done in a furnace or kiln reactor called or calciners with a variety of designs such as shaft furnaces, rotary kilns, multiple hearth furnaces, and fluidized bed reactors. Normally the calcination process was conducted under the melting temperature (melting point) of material products. For limestone, calcination process is generally carried out at temperatures between 900ºC-1000ºC [8].

EXPERIMENTAL SECTION

Equipment and materials research

The tools used in this study is a glass beaker, stirrer motors, furnaces, ovens, spatula, porcelain bowls, glass funnel, thermometer, footage, sieve size of 355 microns, and a porcelain mortar.

The materials used in this study is a waste eggshell, distilled water, sulfuric acid, filter paper.

The variables of this study has fixed variables and variables change. Variable remain present in a concentration of sulfuric acid solution used is 15%. While the change of variables contained in the composition used is the composition of eggshell and distilled water. The mixing ratio which will be tested between eggshell, a solution of sulfuric acid, and distilled water is as presented in Table-4.

Table-4. Mixing ratio of eggshell, sulfuric acid, and distilled water.

No	Sample Name	Composition		
		Eggshell (%)	H_2SO_4 (%)	H_2O (%)
1	G1	20	15	65
2	G2	25	15	60
3	G3	30	15	55
4	G4	35	15	50

Raw material preparation

Raw materials such as eggshell is cleaned and dried, then crushed with a porcelain mortar and then sieved with a sieve size of 355 microns.

Manufacture gypsum

Egg shell waste as much as 1 kg which has been sieved calcined with a furnace at 900 OC for 1 hour. After calcination, then shell gypsum is used with a composition based on the variables used (variable 1 = 200 g; 2 = 250 g variable; variable 3 = 300 g; variable 4 = 350 g) diluted with aquadest to a particular composition based on the variables used (variable 1 = 650 ml; variable 2 = 600 ml; variable 3 = 550 ml; variable 4 = 500 ml) was then added a solution of sulfuric acid (15%, 150 ml). Previous sulfuric acid used diluted from concentrations of 97% to a concentration of 15%, ie by mixing sulfuric acid 97% by volume of 23.19 ml with distilled water volume of 126.80 ml. The third ingredient mixture is stirred with a speed of 250 rpm until the precipitation of gypsum. Gypsum precipitate obtained was filtered with filter paper and dried in an oven at a temperature of 40 ° C for 4 hours, and then weighed.

Analysis

According to [9] Scanning Electron Microscope (SEM) is an equipment used to observe the surface of the material / specific materials in order to get a more detailed (micro and macro structure of the material). This tool is similar to a microscope which we have known since elementary school that Light Microscope. However, the difference with the light microscope is that the Electron Microscope or Scanning Electron Microscope (SEM) has a resolution (0.1 to 0.2) nm while light microscopes are only able to reach 200 nm. In other words magnification using SEM tool is able to reach thousands of times magnification, but by using a light microscope only to just under 300 times magnification.

The working principle of the SEM are as follows:

a. An electron gun produces an electron beam and accelerated by the anode.
b. The magnetic lens focusing electrons toward the sample.
c. The focused electron beam scanning (scanning) the entire sample with coil directed by the scanner.
d. When the electrons on the sample, the sample will issue a new electron to be received by the detector and sent to the monitor (CRT).

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According to [10] X-Ray Diffraction is one technique to structure an analysis of minerals, salts, metals, and even organic compounds such as DNA, vitamins and drugs. If you want to know what materials are contained in a mineral, this technique is quite appropriate because the XRD can provide information about the molecular shape and at what angle the crystal. XRD general working principles are as follows: XRD consists of three main parts that is the X-ray tube, place the object under study, and the X-ray detector X-rays generated in the X-ray tube that contains the heating filament cathode, thus generating electrons. Acceleration voltage difference causes electrons to be fired at the object. When the electrons have a high energy level and electrons bumping into an object so that the resulting X-ray beam and detector rotates objects to capture and record the intensity of X-ray reflection detectors to record and process the X-ray signals and process them in graphical form.

Eggshell and gypsum were analyzed chemical content of each, for example, more the number of levels of $CaCO_3$, CaO, SO_3 in the gypsum made with test methods XRD and SEM test to determine the morphological structure of the eggshell and gypsum. For analysis of the results of the strength of gypsum with material hardness testing using the compressive strength test method CBR (California Bearing Ratio).

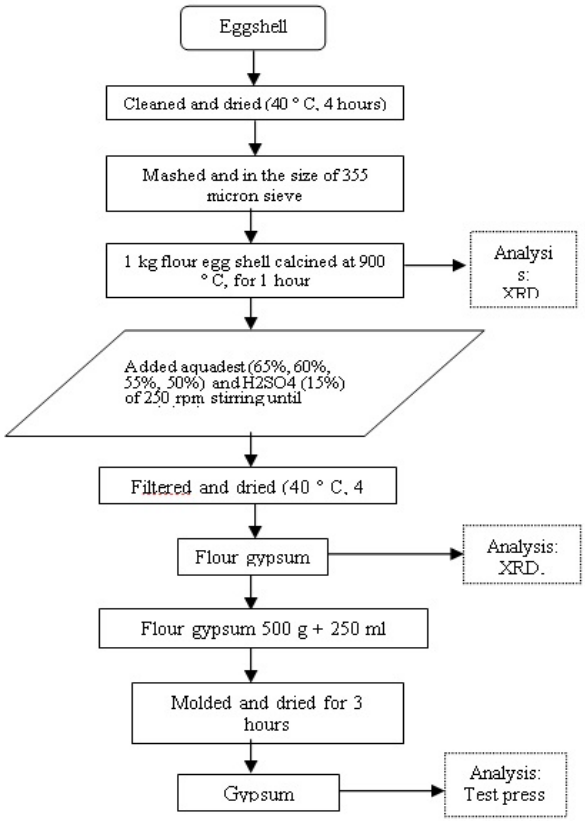

Figure-1. Flow diagram of the manufacturing gypsum and analysis.

RESULTS

Figure-2. (a) The shell eggs, and (b) eggshell after calcination.

Samples calcined eggshell after weighing less than 1 kg into 657 grams, this is due to decomposition and release of CO_2 from the compound $CaCO_3$ compounds contained in an eggshell into CaO that the equation is as follows:

$$CaCO_3 \longrightarrow CaO + CO_2 \quad (1)$$

Based on observations eggshell color change of the sample after calcination is initially white and becomes white-black. This is due to the ash content of organic material contained in the eggshell itself so the color is so [11].

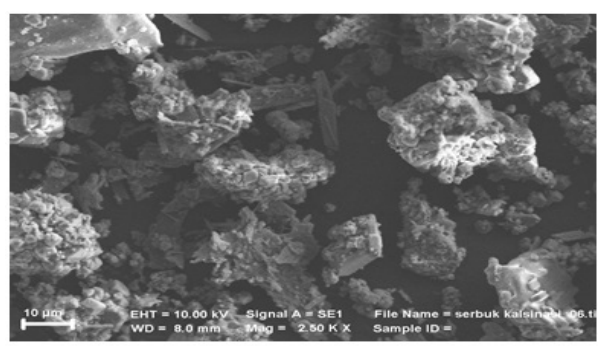

Figure-3. SEM sample test results eggshell after calcined.

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SEM test results of samples calcined eggshell after showing the structure of the surface morphology of the amorphous form still looks rough. This is due to CaO molecule bound between one and the other. To determine levels of CaO contained in the sample eggshell XRD test and the results are as shown in Figure-4.

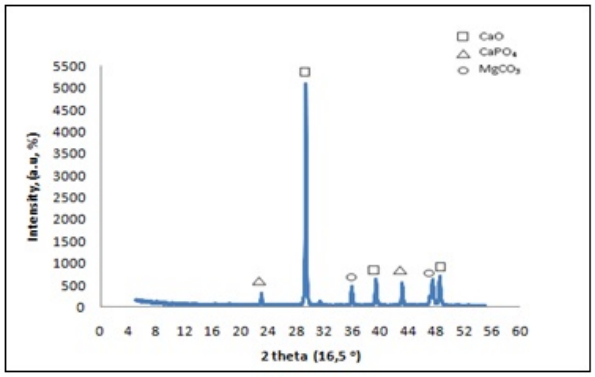

Figure-4. XRD graph of test results eggshell after calcination.

From the graph shows the percentage of CaO contained in the sample the more dominant eggshell that is 42.10%, the rest are organic compounds such as calcium phosphate and magnesium carbonate of 5.45% to 12.5%. CaO compound content is critical to the process of making gypsum (CaSO4.2H2O) because it contained more CaO content the better the quality of the gypsum [11].

Manufacture of gypsum

Samples calcined eggshell was further processed into gypsum by mixing distilled water and sulfuric acid were divided into 4 variables, variables fixed is 15% sulfuric acid and 75 ml of the independent variables are the composition of eggshell and distilled water. The variables are presented in Table-5:

Table-5. Manufacture gypsum composition ratio and the results obtained.

No	Sample Name	Composition			Result	
		Eggshell (%)	H_2SO_4 (%)	H_2O (%)	Weight (gram)	Level (%)
1.	G1	20	15	65	224,5	- O_3 =10,56 - CaO = 60,90 - H_2O = 19,48
2.	G2	25	15	60	396,18	- SO_3 = 2,55 - CaO = 31,96 - H_2O = 4,3
3.	G3	30	15	55	480,14	- SO_3 = 0,22 - CaO = 22,36 - H_2O =0,78
4.	G4	35	15	50	600,2	- SO_3 = 0,48 - CaO = 7,68 - H_2O = 0,98

In the first variable (G1) used samples calcined eggshells with 20% which is 200 g then mixed with aquadest composition of 65% which is 650 ml homogenized in a glass beaker and the solution is mixed with sulfuric acid composition of 15% which is 150 ml. Weight gypsum precipitate obtained dried as much as 224.5 grams, an increase in the weight of the compound before it is due to sulfuric acid and distilled water was mixed into the gypsum itself. The mixing reaction is as follows:

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad (2)$$

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4.2H_2O \quad (3)$$

To know more clearly the composition and structure of morphology whatever is in the gypsum variable 1 is then tested XRD and SEM test results are as shown in Figure-5 and Figure-6:

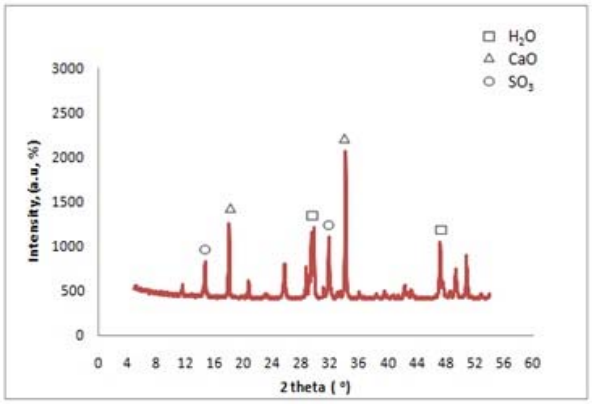

Figure-5. XRD test chart gypsum variable 1

Based on Figure-5, obtained the first variable composition produces gypsum SO3 10.56%, CaO 60.90%, 19.48% H2O. CaO composition in the first variables decreased when compared to the egg shell after calcination this is due to the reaction mixture of distilled water and sulfuric acid to form gypsum (CaSO4.2H2O).

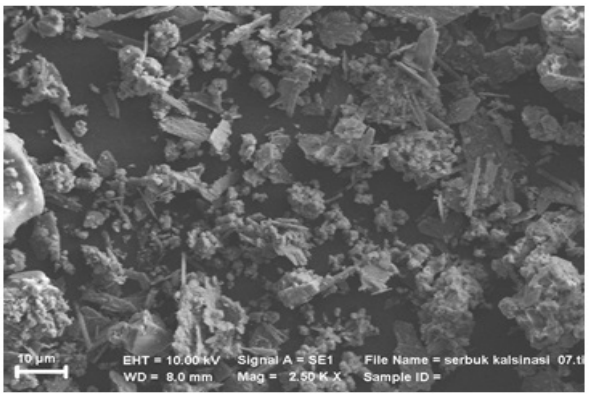

Figure-6. Gypsum SEM test variable 1.

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SEM images gypsum test variable 1 at Figure-6 shows the structure resembles the morphology of needle-shaped crystals has been in accordance with the structure of gypsum crystal morphology. Gypsum morphological structures form variable 1 changes compared with the morphological structure of the eggshell after previously calcined amorphous form, this is due to mixing distilled water and sulfuric acid to break down the amorphous structure of the eggshell after calcination into gypsum crystal grains [12].

In the second variable (G2) Weight of dry gypsum obtained as much as 396.18 g, with SO3 levels of 2.55%, CaO content of 31.96%, H2O content of 4.3% by weight gypsum an increase of gypsum variable 1 this is because the acid compound sulphate and distilled water was mixed into the gypsum itself.

To know more clearly the composition and structure of morphology whatever is in the gypsum variable 2 is then tested XRD and SEM test results are as shown in Figure-7 and Figure-8:

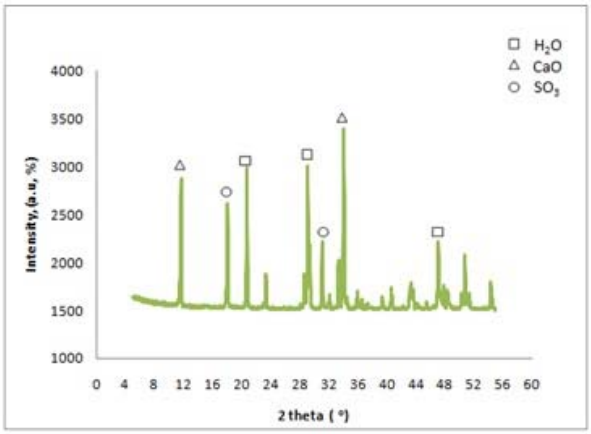

Figure-7. XRD test chart gypsum variable 2.

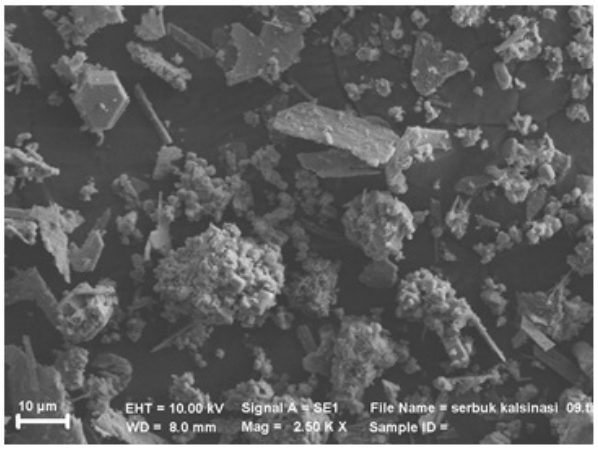

Figure-8. Gypsum SEM test variable 2.

In the third variable (G3) used samples calcined eggshell with a composition of 30% that is 300 g then mixed with aquadest composition of 55% that is 550 ml homogenized in a glass beaker and the solution is mixed with sulfuric acid composition of 15% that is 150 ml. Weight gypsum precipitate obtained dried as much as 480.14 g, with SO_3 levels of 0.22%, CaO content of 22.36%, 0.78% H_2O content of an increase in weight of gypsum from gypsum variable 2, this is because the compound sulfuric acid and distilled water was mixed into the gypsum itself.

To know more clearly the composition and structure of morphology whatever is in the gypsum variable 3 is then tested XRD and SEM test results are as follows:

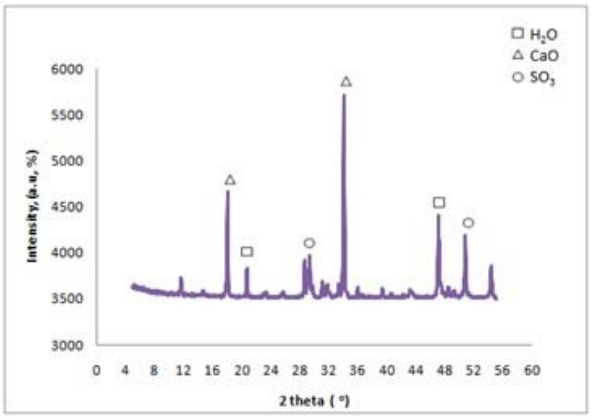

Figure-9. XRD test chart gypsum variable 3.

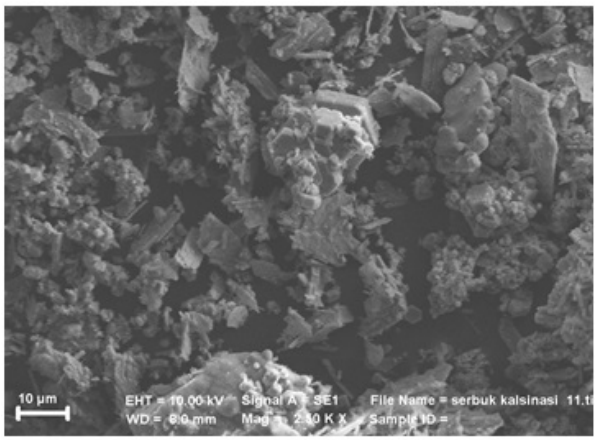

Figure-10. Gypsum SEM test variable 3.

In the fourth variable (G4) used samples calcined eggshell with a composition of 35% that is 350 g then mixed with aquadest composition of 50% that is 500 ml homogenized in a glass beaker and the solution is mixed with sulfuric acid composition of 15% that is 150 ml. Weight gypsum precipitate obtained dried as much as 480.14 g, with SO_3 levels of 0,48%, CaO content of 7,68%, 0,98% H_2O content of an increase in weight of gypsum from gypsum variable 3, this is because the

compound sulfuric acid and distilled water was mixed into the gypsum itself.

To know more clearly the composition and structure of morphology whatever is in the gypsum variable 4 is then tested XRD and SEM test results are as follows:

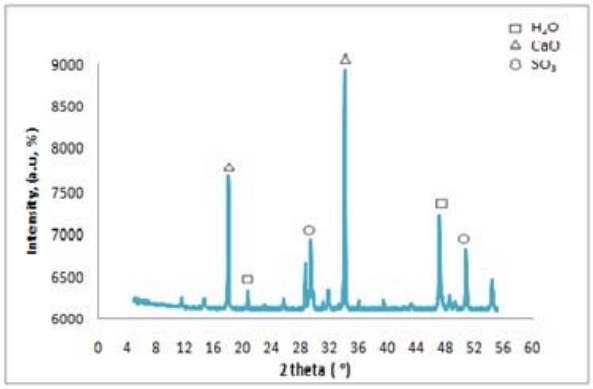

Figure-11. XRD test chart gypsum variable 4.

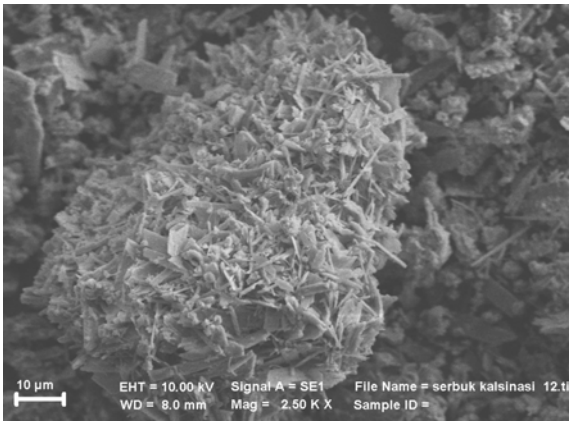

Figure-12. Gypsum SEM test variable 4.

Based on test results of XRD and SEM on several variables gypsum samples showed the most optimal weight of gypsum based on four variables, which is 600.2 g with the ratio of the material composition of eggshell after calcined 35%, 50% distilled water and 15% sulfuric acid while most minimal weight of gypsum contained in the variable 1 is 224.5 g with a ratio of composition of eggshell after calcination 20%, 65% distilled water and 15% sulfuric acid. This is because the amount of egg shells are used so that the ability to absorb liquids by eggshell becomes easier especially absorb distilled water and sulfuric acid, so that got by a more optimal result of gypsum. Several factor that influence making of gypsum are the composition, temperature, stirring, and settling time.

Compressive strength test

At this stage, the compressive strength test on each variable gypsum, first gypsum powder mixed with water into a slurry and then stirred up, then printed with a cylindrical mold. Once printed gypsum cylindrical press test to determine the compressive strength on each variable and compared with gypsum on the market.

Figure-13. Sample gypsum cylindrical.

The results of the pressure tests on gypsum and gypsum market of egg shells are as follows:

1. Gypsum market: Elapse time (7 minutes), load (12.4630 lbs)
2. Gypsum variable 1: Elapse time (1 min), load (0.2783 lbs)
3. Gypsum variable 2: Elapse time (2.5 minutes), load (3.9083 lbs)
4. Gypsum variable 3: Elapse time (4 minutes), load (4.9610 lbs)
5. Gypsum variable 4: Elapse time (5.5 minutes), load (6.5430 lbs)

From the data compression test results we can make a comparison chart gypsum market value of compressive strength with gypsum of eggshells as shown in Figure-14:

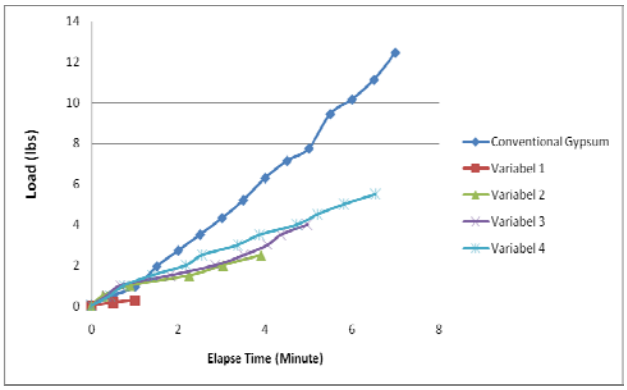

Figure-14. Comparison between the conventional gypsum and gypsum from the research.

Figure-15 shows that the compressive strength gypsum market is greatest and the smallest is gypsum variable 1. This is because the composition of mixing in

the gypsum market is higher than the gypsum from the eggshell. Mixing in the gypsum composition can affect the value of the compressive strength of gypsum.

CONCLUSIONS

Based on the results of the research, it was concluded that comparison of the best composition of eggshell gypsum namely with a ratio of 35% eggshell, 15% sulfuric acid, 50% aquadest produces results that 600.2 grams. The value of the greatest pressure tests on gypsum contained 4 variables namely 6.5430 lbs in Elapse time of 5.5 minutes. Factors affecting the compressive strength of gypsum is gypsum mix composition.

REFERENCES

[1] Pusat litbang Tekmira. 2013. Statistik Gypsum di Indonesia. Informasi Mineral dan Batubara.

[2] Sistem Informasi Sumber Daya Investasi. 2013. Data Produksi Semen Pada Pabrik di Indonesia. Pusat Pembinaan Sumber Daya Investasi.

[3] Gypsum Association. 2007. Application of Gypsum. Gypsum Association 810 First Street NE: Washington, DC.

[4] Wolf, K.H. 1959. Development in Sedimenthology. American Elsevier Publishing Company, Inc: New York.

[5] Dinas Peternakan Provinsi Kalimantan Selatan. 2013. Data Produksi Telur Kabupaten/Kota Kalsel. Livestock Service of Kalimantan Selatan Province.

[6] Butcher, Gary D., Miles, and Richard. 1990. Concepts of Eggshell Quality. U.S. Department of Agriculture.

[7] Hunton, P. 2005. Research on Eggshell Structure and Quality. An Historical Overview, Braz. J. Poult. Sci. 7.67-71.

[8] World Intellectual Property Organization. 2009. Method of Producing Eggshell Powder. America.

[9] Amin. 2013. Strength material advanced. Jakarta.

[10] Yudith. 2010. Analisa XRD, XRF, ICP, AAS, Titrasi atau Gravimetri. Jakarta.

[11] Beckhoff, B. 2010. Compound of Egg Shell, powder XRD. American Elsevier Publishing Company, Inc: New York.

[12] Hoang, T.A., Ang, H.M. and Rohl, A.L. 2007. Effects of temperature on the scaling of calcium lphate in pipes, Powder Technology, 179, 31-37.