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PRETREATMENT OF KAOLIN INTO METAKAOLIN

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ABSTRACT

Most of metakaolin is used in portland cement industries as an additive to improve the compressive strength of the cement. Using Cicalengka and Bangka kaolin as metakaolin raw material, R & D Center for Mineral and Coal Technology found that Bangka kaolin was more suitable in metakaolin preparation because its initial Al_2O_3 content (32.80%) rises up to 37.50% after decantation, meanwhile Cicalengka one can not fulfill the requirements. The non-decanted Bangka kaolin (37.50% Al_2O_3) exceeds the Al_2O_3 content of metakaolin that has been produced commercially by Asian Ceratec Corporation.

Calcination processing follows the decantation one. The decanted Bangka kaolin was then pelletized to have calcining burnt did well. The pellet was burnt in 1 x 0.5 m static laboratory furnace at some temperatures and holding times. Burning temperature of 900^0 C and 20 minutes holding time showed common calcined kaolin characteristic; sheet-like structure, but at some parts it has developed into unregularly thicker sheet structure due to amorphous (non-reactive phase) formation. This phenomenon signs that recrystallization temperature has been achieved and many hydroxil ions has been lost.

Keywords: metakaolin, decantation, calcination

INTRODUCTION

Nowadays, the tremendous constructions; buildings, bridges, highways etc. require high quality cement in a massive quantity. To create a high quality of cement, it should be considered, some of them is the raw material. Most of metakaolin is used by portland cement industries as an additive to improve the compressive strength of the cement. According to Smiley et al (1998), replacing 8.1% of cement by metakaolin and adding slightly more water, the compressive strength of the modified portland cement is the same as the non-modified one after seven days, and higher than the non-modified one after 28 days (73.3 MPa to 64.4 MPa).

This is a preliminary research to serve metakaolin derived from kaolin pretreatment. Being as an additive, metakaolin enhances the physical characteristic of the cement portland. To prepare metakaolin, it needs kaolin as raw material. Kaolin is a clay mineral with chemical composition of $Al_2Si_2O_5(OH)_4$. It is layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina. Kaolin-type clays undergo a series of phase transformations upon thermal treatment in air at atmospheric pressure. Endothermic dehydroxylation (or alternatively, dehydration) begins at 550-600 °C to produce disordered metakaolin, $Al_2Si_2O_7$, but continuous hydroxyl loss (OH^-) is observed up to 900 °C and has been attributed to gradual oxolation of the metakaolin (Niroumand and Kassim, 2010). Usually, natural kaolin can not fulfill the metakaolin preparation requirements yet so that it has to be processed to reach mininum Al_2O_3 content (37.0%). Decantation as part of the kaolin processing series, separate the gangue minerals, e.g. quartz, mica, ferrous mineral, etc.

The qualifying kaolin is then pelletized by means of sodium aluminate binder in 1 x 0.5 m static laboratory furnace at some temperatures and holding times. The calcining temperatures are 600, 700, 800, 900, and 950 °C.

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METHODOLOGY

Research was done at Mineral Centre of Citatah, Western Bandung and Mineral Processing Laboratory of R & D Center for Mineral and Coal Technology. Both of the sites gave primary data such as: chemical composition of natural kaolin (Cicalengka and Bangka), chemical composition of the processed kaolin (decanted kaolin, calcined kaolin), XRD characteristic of the natural and processed kaolin, and photomicrograph of the calcined kaolin. The series of the research activities followed the flow sheet (Figure 1).

The research used Cicalengka and Bangka kaolin as natural minerals. After crushing, scrubbing and screening respectively, decantation was done to separate minerals based on minerals spesific gravity differences. Calcination used two variables; that were 600, 700, 800, 900, and 950 °C for the calcining temperatures and 10, 20, 30 and 40 minutes for the holding times. The calcination was done in 1 x 0.5 m static laboratory furnace to minimize the hydroxil content which is inturn tend to form meta-stable structure of amorphous area.

RESULTS AND DISCUSSIONS

Natural (raw) kaolin processing is aimed to determine the origin of the respected natural kaolin that is suitable for metakaolin preparation, the volume, and the quality of the product. To gain the data, some of tests have been done such as raw material characterization, screening, settling/decantation, hose-used water disposal and calcination.

Mineral Composition

Based on XRD test, the raw material contained kaolinite and other gangue minerals, which consists of quartz (tridymite), and feldspar (sanidin) for Cicalengka kaolin basis and potassium aluminium silicate hydroxide and aluminium silicate for Bangka kaolin basis (Figure 2 and 3).

Chemical Composition

The quality of Bangka kaolin is better than that of Cicalengka one for metakaolin preparation purpose. Comparing to pure kaolin that contains 46.54% SiO_2, 39.56% Al_2O_3 and 13.90% H_2O (Grimshaw, 1971), Cicalengka kaolin is higher in SiO_2 content than pure kaolin because of the existing quartz, and is higher in Na_2O because of the existing potassium sodium-type feldspar (sanidine). Chemical composition of raw material can be seen in Table 1. Both of Cicalengka and Bangka kaolin contain Al_2O_3 18.94 % and 32.80% respectively that are less than pure kaolin.

Grain Size Distribution

The samples' grain size distribution is depicted in Table 2 and Figure 4. It contained amount of coarse fractions: +60 mesh (12.61%), -325 mesh (63.32%) and fraction less than 2 micron (4800 mesh) is 10,16%. According to this distribution, the kaolin has met the metakaolin's raw material spesification (Smiley et al, 1998); e.g. almost 50% of the overall weight approaches 2400 mesh (5 microns) particle size or less and almost 10% approaches 4800 mesh (2 microns) or less.

Trommol Screen Separation Test

Used as raw material, Bangka kaolin contained amount of coarse fraction in form of sand and gravel. The coarse fraction separation causes the increase of kaolin content because it has very fine size; less than 5 microns. Separating the coarse fraction (+60 mesh) by means of *trommol screen* is the initial stage of the present kaolin processing.

The percentage of dried weight fraction of -60 mesh to the initial feed measured at the test was be-

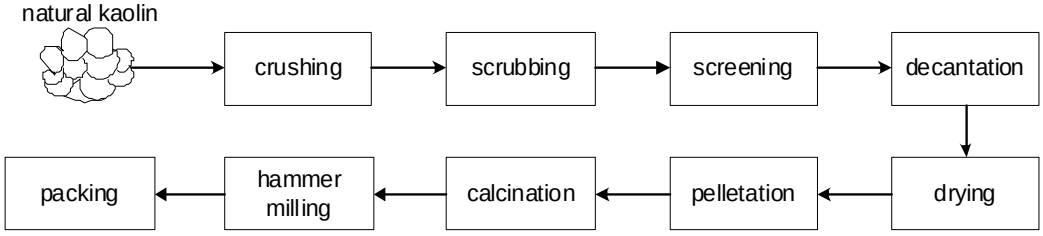
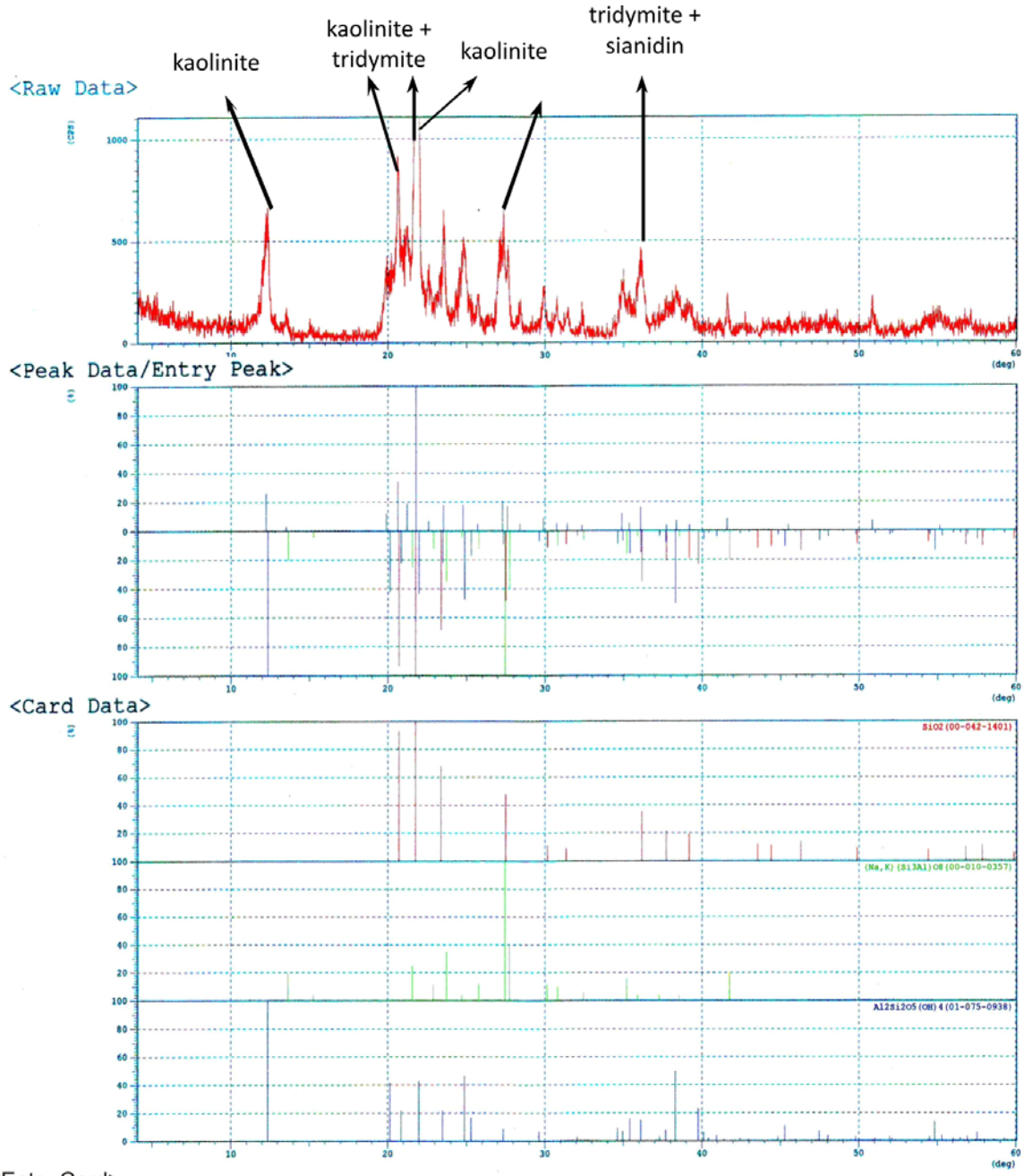


Figure 1. The flow diagram of the metakaolin preparation



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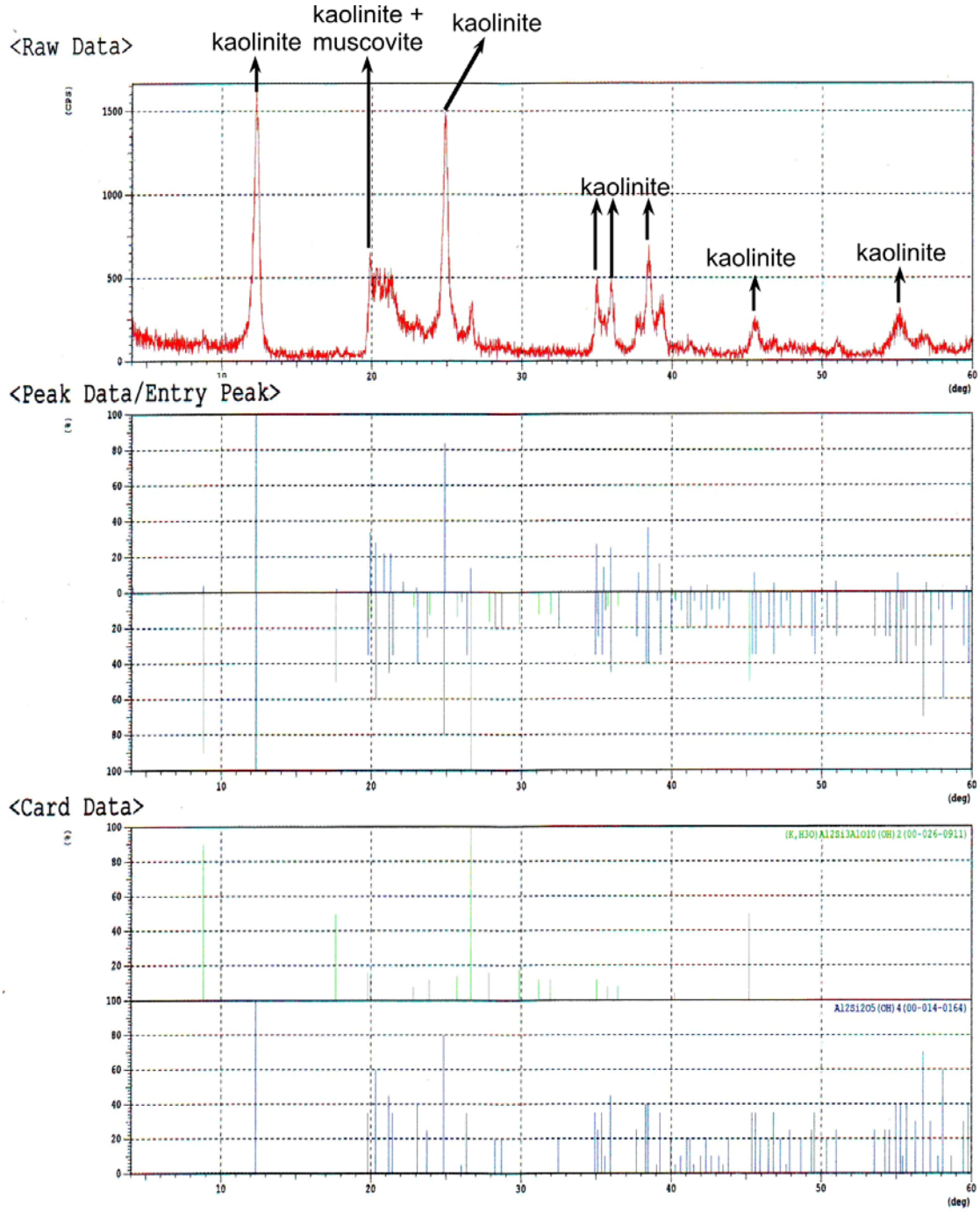
No.	Card	Chemical Formula Chemical Name (Mineral Name)	S	L Dx	WT %	d S.G.	I	R
1	00-042-1401	SiO_2 Silicon Oxide (Tridymite-O)	0.512	0.529 2.45	(9/23)	0.821	0.595 F	0.2
2	00-010-0357	$(Na,K)(Si_3Al)O_8$ Potassium Sodium Aluminum Silicate (Sanid	0.430	0.882 2.57	(15/17)	0.634	0.338 C2/m	0.1
3	01-075-0938	$Al_2Si_2O_5(OH)_4$ Aluminum Silicate Hydroxide (Kaolinite SM	1.000	1.000 2.61	(*/189)	1.000	1.000 Cc	1.

Figure 2. XRD diffractogram of natural Cicalengka kaolin showing kaolinite and dominant mineral such as silicon oxide (tridymite) and potassium sodium alumina silicate (sanidin)



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No.	Card	Chemical Formula Chemical Name (Mineral Name)	S	L Dx	WT %	d S.G.	I	R
1	00-042-1401	$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$ Potassium Aluminum Silicate Hydroxide (I1	0.202	0.412 ------	(7/18)	0.741	0.207 C2/c	0.0
2	00-010-0357	$Al_2Si_2O_5(OH)_4$ Aluminum Silicate Hydroxide (Kaolinite-1A	1.000	1.000 2.60	(*/67)	1.000	1.000 C1	1.0

Figure 3. XRD diffractogram of natural Bangka kaolin containing potassium aluminium silicate hydroxide (muscovite) and aluminium silicate hydroxide (kaolinite)

Table 1. Chemical composition of Cicalengka and Bangka kaolin compares to pure kaolin

Origin	Content (%)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	LOI	H_2O
Cicalengka	67.60	18.94	0.63	0.82	0.36	0.22	1.05	0.46	9.92	-
Bangka	44.23	32.80	0.64	0.06	0.19	0.27	ttd	-	14.11	-
pure kaolin	46.54	39.56	-	-	-	-	-	-	-	13.90

Table 2. Raw material's grain size distribution in wet screen analyses using sedimentation method

Fraction/Size (mesh/micron)		% weight	% Weight Cumulative	
Mesh	Micron (ìm)		Retained (%)	Passed (%)
+60	+ 250	12,61	12,61	87,39
-60 + 100	-250 + 149	16,67	29,28	70,72
-100 + 200	-149 + 74	9,99	39,27	60,73
-200 + 325	-74 + 44	9,48	48,75	51,25
-325 + 2400	- 44 + 5	14,57	63,32	36,68
-2400 + 4800	-5 + 2	26,52	89,84	10,16
- 4800	-2	10,16	100	0

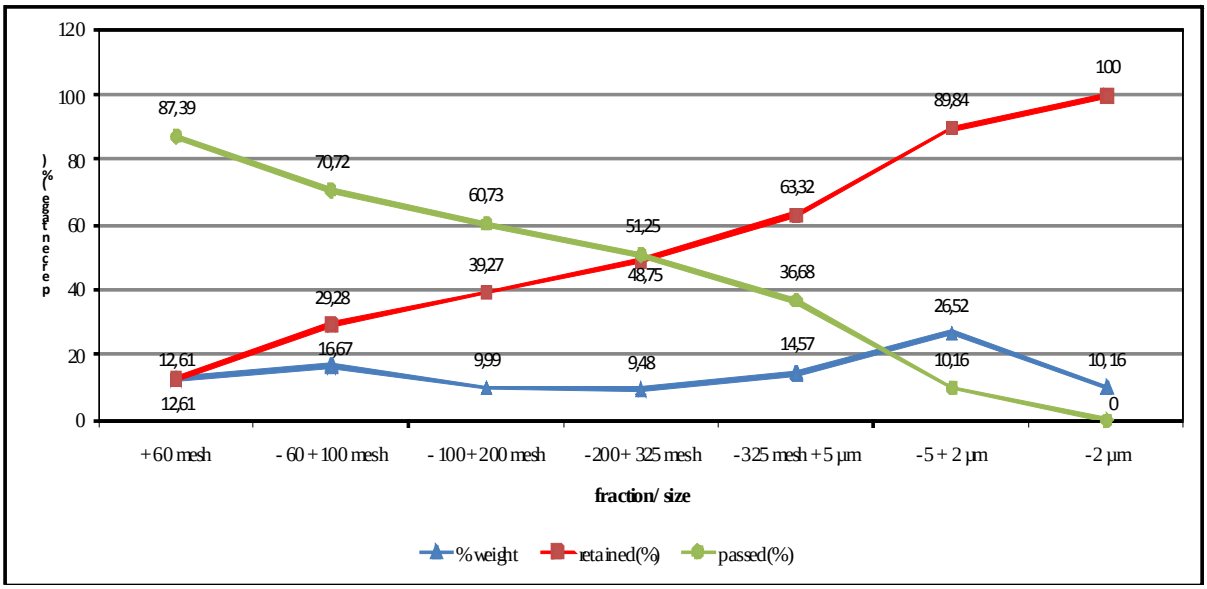


Figure 4. Raw material's grain size distribution in wet screen analysis using sedimentation method

tween 79.46 - 86.25% (Table 3) or 83,88% in average, so that the +60 mesh had 16.12% in average. Referring to laboratory screened result, -60 mesh 87.39% (Table 2), the trommol screen performance is coincided with ratio value 3.88/87.39 or 96% relative to laboratory screened (manual) result.

After analysing grain size distribution (screening analysis), the effect of solid percentages should be considred. The passed fractions of 60 meshes tend to increase in line with the increase of solid percentage (Figure 5). Ratio of dried solid weight to feed weight at the first test seemed not to follow the trend line, because the trommol screen condition had not been stable yet, concerning the initial stage of the trommol screen operation. Theoretically, water is supporting enough to make the screening done well. Water shortage will not re-

Table 3. Ratio of the 60 mesh screen-released solid weight vs feed weight (%) of the Bangka kaolin in trommol screen with the variation of feed solid percentage

Parameter	Tests				
	First	Second	Third	Fourth	Fifth
Inlet					
Initial feeding (wet, kg)	92	128	156	192	220
Initial feeding (dry, kg)	74.6	110	135	165	189
Solid percentage (%)	7.64	10.86	12.98	15.33	17.12
Outlet					
Retained Fraction of 60 mesh					
Wet solid weight (kg)	16	35	36	37	40
Dry solid weight (kg)	11	22,6	23	24	26
Passed fraction of 60 mesh					
Dry solid weight (Kg)	63.6	87.4	112	141	165
Ratio of dried solid weight to feed weight (%)	85.25	79.46	82.97	85.46	86.25

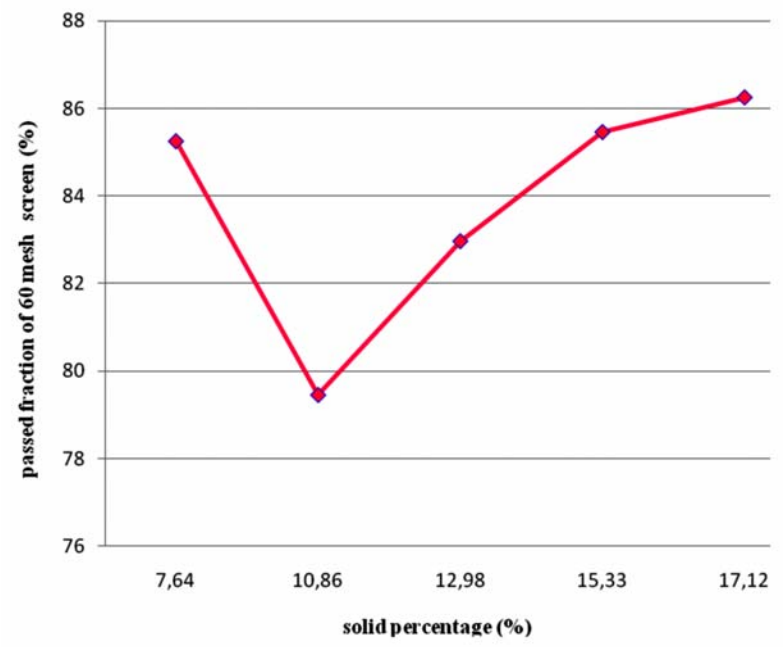


Figure 5. Chart of the effect of solid percentage of the concentrate to feed ratio

lease kaolin from that of impurities such as sand, feldpar, etc. The low solid percentage tends to enhance the screen performance that is indicated by released-solid weight ratio. This percentage was counted based on the releasing weight feed. At higher solid percentage, many of the minerals will be separated untill reach asymptotic at 17 % because the spesific area of the minerals grain size has achieved optimum measurement therefore the passed fraction will almost be constant.

The cross-section area of the screen truly determines the screen capacity. The vibrated-type screen has capacity between 0.2 and 0.8 ton/ft^2-hour-mm-mesh (Mc.Cabe and Smith, 1976). Referring to that study, take 0.2 ton/ft^2-hour-mm-mesh capacity, 60 mesh screen size or 0.250 mm, one hour operation, the screen area for 1 ton feed is 1.25 ft^2. Meanwhile the screen has 31.4 ft^2 gross area and if the assumed effective screen area is 20 % or 6.2 ft^2 so that the screen can theoretically operate for 4.96 ton/hour. In fact, screen can

reach 220 kg feed/5 minutes or 2.64 ton/hour. This is still under the theoretical capacity of the screen. This occured because most of the effective screen area was covered by clumped particle (natural kaolin) during the screen vibration regarding to the formation of optimum solid percentage causing the passed fraction asymptotic.

Separation by Settling Test

Settling/decantation test uses feed that was previously produced by trommol screen. This type of separation works based on the spesific gravity differences of material in thin slurry (Anonym, 2009). Since mica has the lowest spesific gravity, it floates in the thin slurry meanwhile kaolinite is under the mica and quarts is at the bottom part of the slurry. According to Suhala (1997), the spesific gravities data of mica, kaolinite, and quartz can be seen in Table 4.

Table 4. The Spesific gravities of mica, kaolinite, and quartz

Minerals	Spesific Gravity
mica	0.12
kaolinite	2.60 - 2.63
quartz	2.65

The amount of mica is 20 % and kaolinite is 70 %; the rest is quartz. After sucking the mica, kaolinite is inturn. The last suction is for quartz. The decanted Cicalengka kaolin's weight was 1190 g, Bangka kaolin was 500 g, stirred with 10 % solid (4.5 l volume) for 6 hours, then let it be idle for 15 minutes. Based on the process, there are two fractions formed; water and watery kaolin. About 25% of that kaolin was sucked, dried and weighed. Then, the rest was divided into 2 parts. Each part was sucked, dried and weighed.

According to Al_2O_3 chemical composition analyses, there is an increase of Al_2O_3 content. It indicated that separation has succeeded because of a significant difference of grain size or specific gravities' of minerals. The Al_2O_3 content of both Cicalengka and Bangka kaolin increases. The Cicalengka kaolin rises from 18.94 % Al_2O_3 (Table 1) to 21.7 % Al_2O_3 (Table 5) with 10 % recovery whereas the Bangka kaolin rises from 32.80 % Al_2O_3 (Table 1) to 37.50 % Al_2O_3 (Table 5) with 75 % recovery. The descending SiO_2 causes the rise of Al_2O_3 content. The chemical composition and the decanted-kaolin weight is tabulated in Table 5. The graphic of Al_2O_3 content at each weight proportion could be seen at Figure 6.

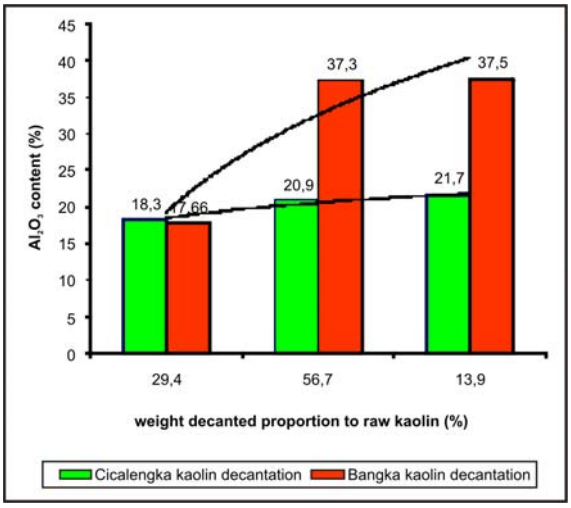


Figure 6. The Graphic of Al_2O_3 content vs decanted-kaolin weight proportion to raw kaolin

Characterization of Decanted Kaolin

Table 5 gives more information about the chemical composition of the decanted kaolin product of

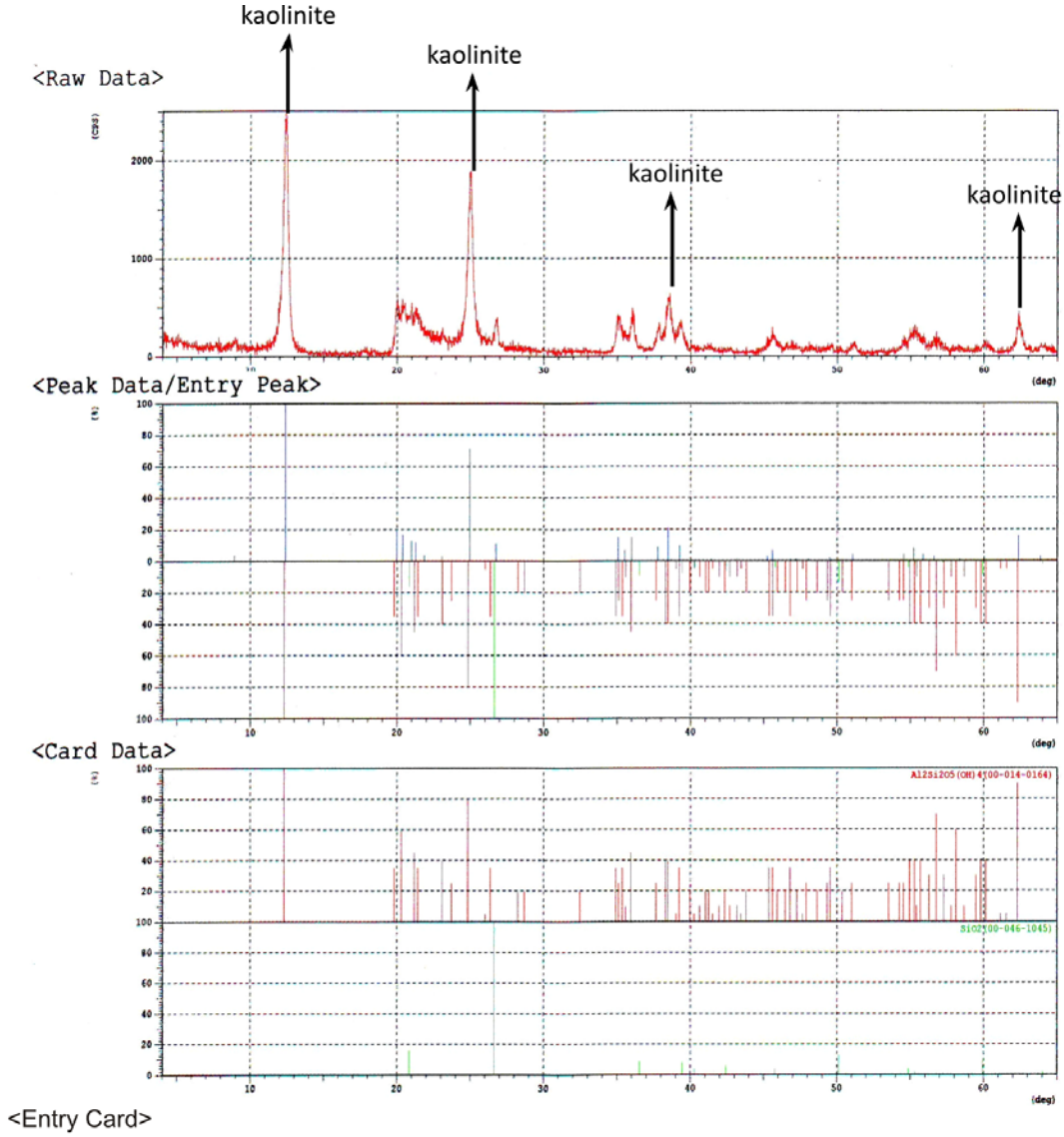
Table 5. The Chemical composition and the decantated-kaolin weight

Kaolin Product	Content (%)				Weight	
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	kg	Weight Ratio to Raw Kaolin (%)
Cicalengka decantation 1	59.8	18.3	-	-	0.350	29.4
Cicalengka decantation 2	60.5	20.9	-	-	0.675	56.7
Cicalengka decantation 3	61.7	21.7	-	-	0.165	13.9
Bangka decantation 1	67.8	17.66	0.46	-	0.110	22
Bangka decantation 2	45.3	37.3	0.56	0.47	0.129	25.8
Bangka decantation 3	45.5	37.5	0.54	0.37	0.261	52.2

trommol screen. Based on Table 5, it inferred that the natural Bangka kaolin (Bangka decantation 2 & 3) is more suitable than Cicalengka one as raw material for metakaolin because its Al_2O_3 content exceeds 35 %; the minimal value of kaolin's Al_2O_3 content in metakaolin preparation. This conclusion was affirmed by x-ray diffraction (XRD) analysis showing that kaolinite mineral clearly exists (Figure 7).

Calcination of Bangka Kaolin Pellet for Metakaolin Preparation

Taking conclusion of the material source of metakaolin, the experiment used the decanted Bangka kaolin as raw material in the next metakaolin preparation.



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No.	Card	Chemical Formula Chemical Name (Mineral Name)	S	L Dx	WT%	d S.G.	I	R
1	00-014-0164	$Al_2Si_2O_5(OH)_4$ Aluminum Silicate Hydroxide (Kaolinite-1A	0.321	0.403 (27/67) 2.60		0.720	0.431 CI	0.1
2	00-046-1045	SiO_2 Silicon Oxide (Quartz, syn)	1.000	1.000 (*/67) 2.65		1.000	1.000 P3221	1.0

Figure 7. XRD diffractogram of the processed natural Bangka kaolin

Calcination was done in laboratory scale with temperature and time variable. Sodium aluminate was used as binder. The folowing Table 6 is the chemical composition of sodium aluminate.

Table 6. The chemical composition of sodium aluminate as binder in pellet making

Sample Type	% Al_2O_3	Al_2O_3 mg/ml	% Na_2O	Na_2O g/l
solution	-	12.26	-	50.1
solid	29.8	-	3.25	-

The calcining temperature was set severely at: 600, 700, 800, 900, and 950^0 C. At each temperature, the samples were calcined for 10 , 20, 30, and 40 minutes in 1 x 0.5 m static laboratory furnace. To understand the micro structure of the calcined sample, XRD and x-ray mapping were done using 20 minutes-burned sample at each temperature. Therefore, the samples used for laboratory analysis were 4 (four) pieces, but only one of the samples was analysed by x-ray mapping. The calcined sample burned at 950^0 C for 20 minutes was used as referrence temperature that is considered close to critical temperatures (975^0 C) (Smiley et al, 1998) where kaolin tends to form amorphous structure indicating recrystallization has happened.

The micro structure of the calcined kaolin could be seen at Figure 8, compared to the uncalcined kaolin at Figure 9. X-ray mapping showed that the calcined sample had a heap of sheet, so that the kaolin plate structure changed from thin into the thick one which was thicker than one before being calcined and it figured out the irregular heap of sheet. This phenomenon indicates the formation of amorphous area. According to Mitra (1969) kaolinite mineral has many of thin, regular layers of plate and resembles sheet of books' pages. The structure change was caused by the lost of hydroxil ions so that only a small portion of the powerfull hydroxil bounds left. This theory is supported by Varga (2007). According to Varga (2007, 7) dehydroxylation is a reaction of decomposition of kaolinite crystals to a partially disordered structure. If the calcining temperature rose to 975^0 C it will cause recrystallization which was indicated by non-reactive phase formation (Smiley at all, 1998, 8). Still from x-ray mapping, it also determined the chemical composition of the calcined kaolin with the following values: 49.12% Al_2O_3, and 50.88% SiO_2. These values were the result of the x-ray mapping analysis that can be seen at Figure 10 taken from the laboratory test.

Still from the laboratory test, XRD analysis showed that Figure 11 ilustrates metakaolin structure has been formed, based on Al and Si elements' peak of the curve.

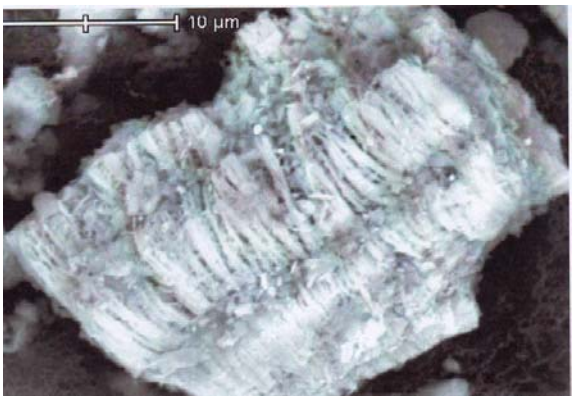


Figure 8. The micro structure of the calcined kaolin at 900°C for 20 minutes roasting

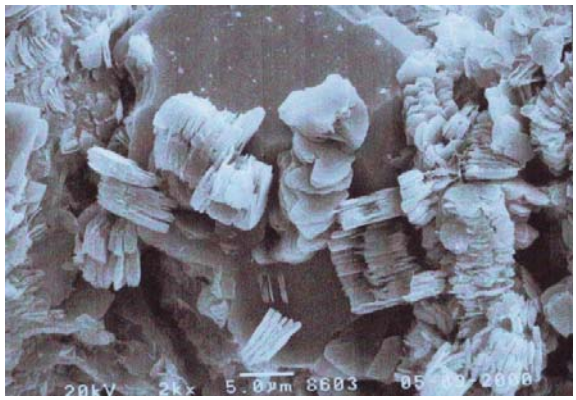
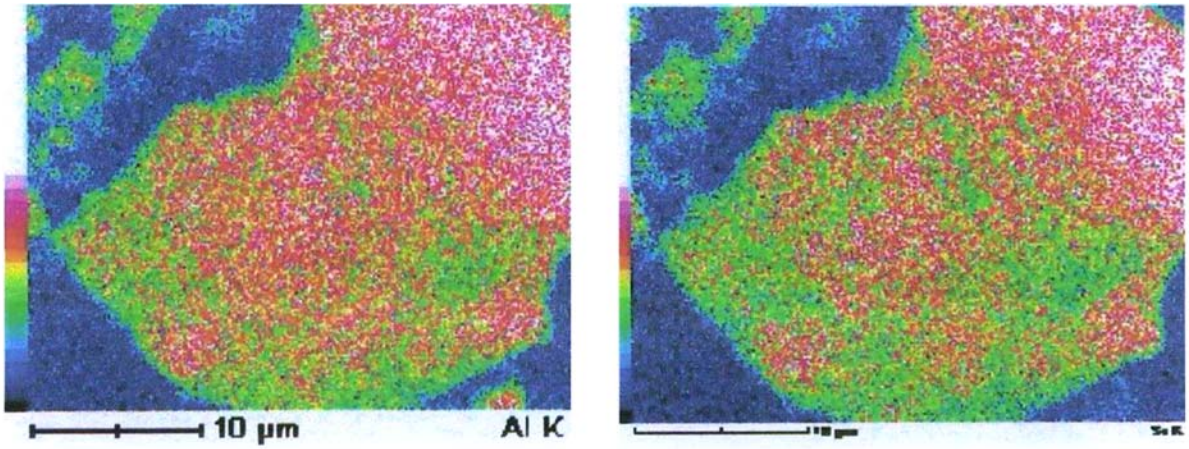


Figure 9. The micro structure of kaolin before being calcined (source: www.omnilabs.com)



Element	(keV)	mass%	Error%	At%	Compound		mass%	Cation	K
O		50.22							
Al K	1.486	26.00	1.05	36.26	Al2O3	49.12	7.37	56.7872	
Si K	1.739	23.78	1.40	63.74	SiO2	50.88	6.47	43.2128	
Total		100.00		100.00		100.00	13.84		

Figure 10. The metakaolin elements of the x-ray mapping based analysis

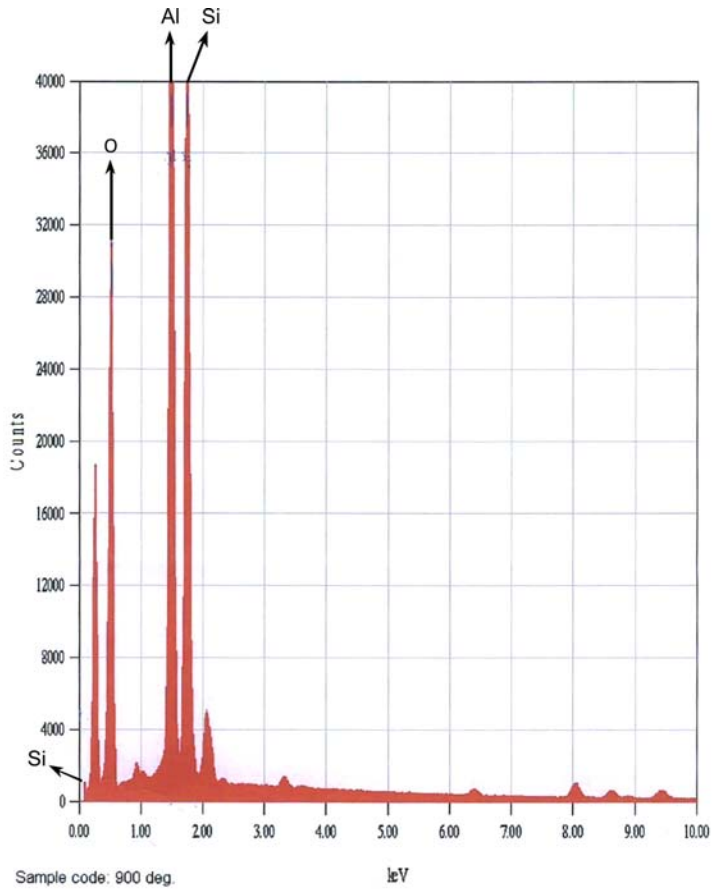


Figure 11. Specton of metakaolin, derived from x-ray mapping (SEM-EDS, shows the elements peak of Al and Si)

Table 7. Standar Property Metakaolin (Meta Fume), Dried Kaolin – Asian Ceratec Corporation (http:/www.ecplaza.net/product/256114-9473/metakolin-metafume.html)

Product	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)
Metakaolin	53,0	38,0	2,5
Dried Kaolin	46,0	35,0	2.7

The Al_2O_3 and SiO_2 contents (Figure 10) are quite close to Asian Ceratec Corporation's product (Table 7). Asian Ceratec Corporation is a metakaolin-based company which has commercially sold metakaolin in the worldwide.

According to Smiley at all (1998, 4-5, 8), calcined kaolin-based metakaolin preparation succeeded as portland cement additive, if the calcined kaolin forms meta-stable material (amorphous area) with low hydroxil content and 0.4 to 0.6 % ignition loss. Ignition loss is a measure of the rest kaolinite, and hydroxil in metakaolin that's just come out from the furnace or kiln.

CONCLUSION

The initial research of metakaolin preparation using the natural Cicalengka and Bangka kaolin in R & D Center for Mineral and Coal Technology gives conclusion as follows:

1. Coming out from the trommol screen, both Cicalengka and Bangka kaolin were raw materials for settling/decantation test. The decanted Cicalengka and Bangka kaolin's weight were 1190 g and 500 g respectively.

2. Cicalengka natural kaolin contains quartz and kaolinite whereas Bangka natural kaolin contains mica and kaolinite.

3. Cicalengka natural kaolin can not be processed into metakaolin's raw material because the dried kaolin can only reach content can only reach 26.80 % of Al_2O_3 with 10 % recovery meanwhile Bangka natural kaolin can be processed into metakaolin's raw material because the dried kaolin reaches 37.5 % of Al_2O_3 with 75 % recovery. 37.5 % Al_2O_3 exceeds the minimal value of Al_2O_3 content that is globally marketed by Asian Ceratec Corporation in their dried kaolin product (35 % Al_2O_3).

4. The calcined kaolin showed the typical metakaolin depicted by x-ray mapping with 49.12 % Al_2O_3 that was exceeding the minimum value of Al_2O_3 content that is globally marketed by Asian Ceratec Corporation in their metakaolin product (38 % Al_2O_3).

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