

## CHAPTER 7

### DISCUSSION OF RESULTS

#### 7.1 General Characterization of Ball Clays

##### 7.1.1 Chemical Composition

From Table 6.1, the ball clay with highest  $\text{Al}_2\text{O}_3$  content is KK which is also low  $\text{SiO}_2$  content that confirm to mineral composition (by XRD), which is also KK has high disordered kaolinite and lowest quartz. The other is HVC also with high content of  $\text{SiO}_2$ , consequently, HVC has high medium disordered kaolinite and moderate content of quartz. Considering the amount of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , MS and REX are very closely similar. Although their difference in LOI and vast different of  $\text{TiO}_2$  indicate that MS has higher  $\text{Fe}_2\text{O}_3$  between the two. On the other hand, REX has higher  $\text{TiO}_2$  than MS. If we consider MS and REX in term of mineralogy they look completely different because MS has disordered kaolinite and some of mixed layer mineral partly expandable with glycol but REX has medium disordered kaolinite and some of mixed layer mineral non-expandable with glycol. In addition quartz contents also different.

Examination of LOI content, ball clay with the highest LOI is PC and followed by MVW, SB-75 and HVC, respectively. This indicates the trend of having good plasticity (from organic content) the fact that MVW is beings used in tableware industry (Jiggering process). The lowest LOI ball clay is MT which is being utilized in the tile industry for fast firing process. REX and JK have the same level of organic matter.

### 7.1.2 Mineral Composition

Fig.6.1 and 6.2 show the qualitative mineral analysis. Table 6.2 reported quantitative mineral analysis of imported ball clays which consist of medium disordered kaolinite whilst local ball clays have only disordered kaolinite. In group I ball clay, MT has the lowest content of disordered kaolinite and maximum quartz amount and group II ball clay look the same in type of composition except BB. It has dominant moderately crystalline muscovite mica at 11 % which is resulting in high casting rate and mixed layer mineral partly expandable with glycol. On the contrary the remainder are mixed layer minerals non-expandable with glycol. The BB also has highest quartz content.

For all samples KK has highest content of kaolinite; however, it is in the form of disordered kaolinite. It also has lowest quartz and some of mixed layer mineral expandable with glycol. The minor constituent is albite, which only presents in REX and rutile is in SB-75, REX and BB. HVC has 1 % of anatase. As a result, we can concluded that all local ball clays consist of disordered kaolinite whilst all imported ball clays are moderately disorder kaolinite.

### 7.1.3 Microstructure by

#### 7.1.3.1 Scanning Electron Microscope(SEM)

Fig.6.3 to Fig.6.13 show electron micrograph of ball clays in this study have been investigated by SEM (-60 # mesh before grinding for sample preparation) at 20,000 magnification. MS(Fig.6.1), MVW(Fig.6.2) and MT(Fig.6.3) from the same mining area seem to have the same particle

shape And the edge is round which has not shown in pseudo-hexagonal nature. MT has smaller particles size than the others in this group. SB-75(Fig.6.6), HVC(Fig.6.7), REX (Fig.6.8) and BB(Fig.6.9) in group II ball clay seem to have smaller particle size than group I but similar in particle shape which sharp edge is not visible. Particle size  $< 0.5 \mu\text{m}$  is the most common size in this ball clay group. The thickness of the particles are similar for those both group I and II.

JK in Fig.6.10 has the thinnest plate of particle resulting in high slippery when it is wet. KK(Fig.6.11), WN (Fig.6.12) and PC(Fig.6.13) in group III show the same microstructure for SEM appearance, which is completely different from group II, JK and group I. These ball clays have finer microstructure, which mostly lesser than  $0.4 \mu\text{m}$  in particle size.

#### 7.1.3.2 Transmitted Electron Microscope(TEM)

Group I ball clay as MS MVW and MT in Fig.6.14-6.16, they are similarly show pseudo-hexagonal shapes, since they came from the same mining area. SB-75, HVC, REX and BB show in the Fig.6.17 through Fig.6.20 in group II have the evidence of the pseudo-hexagonal shape particle especially BB. Similarly the Table 6.2 show that this group have medium disordered kaolinite, so we can expect to see more pseudo-hexagonal shape when they are investigated by TEM. This leads to the fact of high casting rate of BB. Group III look familiar to group I in shape but absolutely different in particle sizes. Because of their absent of ordered kaolinite structure, the examination by TEM will not reveal the obviously pseudo-hexagonal structure.

### 7.1.4 Particle Size Distribution

Fig.6.25 and Table 6.3 illustrate residue particularly residue on 120 #. We can see MVW residue consists of high lignite and low quartz which result in black color. MT has lesser lignite and more quartz, thus yield lighter color. MS has all lignite, quartz subsequently shows its residue color between MVW and MT. Because of its lowest lignite, MT is the most suitable for tile industry. Even its 200 #, 325 # residue, MVW still shows higher lignite content. However MS and MT have some amount of micas and quartz instead of lignite. As for imported ball clays group II, HVC (Fig.6.26) and BB in Fig.6.27 have residue on 120 # as lignite and some quartz. Their content still have more lignite than MS. SB-75 (Fig.6.26) has quartz sand on 120 # but show dark color residue on 325 #, which seem to have finer lignite residue than the others. REX has most white residue on 120 #, 200 # and 325 #. Its 120 # residue shows some amount of micas evidently. Group II among the local ball clays, WN residue on 120 # contains organic and some micas in the finer residue fraction. While its 325 # residue, fine silica has been observed. JK (Fig.6.28) has a residue color of yellow. There is also some amount of quartz but no trace of micas in the JK. KK residue which is reddish brown in color, has no sign of quartz or micas. This reddish brown appearance is from its organic compound. Fig.6.29, PC residue has deep grey to black color. Its component still consists of a little amount of quartz and micas and the rest is clay with organic particles.

The particle size distribution at  $-20\ \mu\text{m}$ , which has been tested by Sedigraph, is being shown in Table 6.3. These results show that the finest particle size distribution is KK, follow by JK, PC, SB-75 and MVW. Considering particle size

at  $-2 \mu\text{m}$ , because of its finest in group I (Mae Than ball clay), MVW is the most suitable ball clay for tableware. MVW has the particle size distribution familiar to HVC. SB-75 has almost its distribution similar to JK's. At colloidal size of  $-1 \mu\text{m}$ , all KK, PC, SB-75 and JK show to have more than 70 % of their particle size is smaller than  $1 \mu\text{m}$ . Thus we should expect more plasticity property from them. In addition, KK and PC show to have the highest content of  $-0.2 \mu\text{m}$  particle. When consider at the  $-2 \mu\text{m}$  particle size, KK is the finest one.

Among the group II ball clays, SB-75 is the finest, which comprise mostly with  $-0.2 \mu\text{m}$  particle. The coarsest ball clay is REX. However, when considering at  $-2 \mu\text{m}$ , all HVC, REX and BB appear to be similar.

## 7.2 Organic Matter

Table 6.4 shows the content of organic matter in the form of TC, IC, OC, humic acid,  $\beta$ -humus accordingly the last row is percentage of humic substance (humic acid and  $\beta$ -humus) determined by organic carbon which is the amount of effective humic substance presented in the organic part of ball clays.

From this table the highest content of TC is MVW, following by SB-75 and HVC (at the level of 2% and above). OC level also have the same portion. It is noticeable that all of TC content in SB-75 and HVC is OC while MVW has more IC than SB-75 and HVC. Level of IC is higher in MVW than both SB-75 and HVC. All of WN, PC, KK have the level of TC at 1.5-2.0 % but only WN has low content of IC. REX has the lowest content of TC and OC and follow by JK. From the group I, MT has very low TC content which conformed to the utilization of MT in tile industry. MVW has the highest amount of TC and so is suitable for tableware factory. Because they

need jiggering process which require the high plasticity property of MVW. Crucial information derives from this table is that ball clays in group I have lower humic acid than any others in group II.

In term of humic substance content, both SB-75 and BB have the highest level. When we consider percentage humic substance in term of OC, BB obviously shows almost all of all OC as active humic substance (humic acid and  $\beta$ -humus). BB also has high  $\beta$ -humus similar to KK, WN and PC in group III. According to the theory of rheology and casting properties, which concern mainly on humic substance especially the humic acid. We found that MS has the lower level of OC, humic acid and humic substance percentage than all imported ball clays (group II). KK, WN and PC has high content of both humic acid and IC. JK look remarkably similar to REX because of their very low TC content. Almost all those TC are OC as mostly are humic substance. Although MVW comprise of high OC but with low portion of humic substance.

Fig.6.30 to 6.40 show extractable humic substances as humic acid,  $\beta$ -humus and fulvic solution from all ball clays used in this study. These humic acid and  $\beta$ -humus are brown in color, fulvic solutions are vary from pale yellow to brownish yellow these appearances seem reflex the identification character of ball clays since they look differ from one's to another's. Group I ball clay as MS(Fig.6.30), MVW(Fig.6.31) and MT(Fig.6.32) look similar in color of yellowish brown color of humic substances. Group II, both SB-75(Fig.6.33) and HVC(Fig.6.34) appear to be the same in color of humic substance. However they are different in color from BB's (Fig.6.36) and REX's (Fig.6.35). Both BB humic acid and  $\beta$ -humus color are brown in color, on the other hand fulvic

solution is 'off white' color. REX are yellowish brown in color humic acid and  $\beta$ -humus. REX has also most pale color of fulvic solution of all ball clays, consequently it has most pale color of residue. Some samples of  $\beta$ -humus show to have yellow in color for example the JK in Fig.6.37. Some of them also show deep brown humic acid color as the PC in Fig.6.40. Besides, their colors are related to residue color. JK yield yellow-pale orange color residue as indicated similar color of humic acid and  $\beta$ -humus has orange-yellow color too. KK (Fig.6.38) has reddish brown residue color which reflected to the color of humic acid,  $\beta$ -humus. KK has reddish brown color of humic substance as well as its residue color. Where as PC has deep gray color of residue as brown to black color of its humic substance. It also revealed that the ball clays with high percentage of humic substance as OC will have light color of fulvic solution. They yielded no organic substance in the last filtrate.

Fig.6.41 and 6.42 show NMR identification of extractable humic substance. In Fig.6.41 when emphasis all the peak of  $\text{CH}_2$ ,  $\text{CH}_3$  at 20-40 ppm, benzene ring at 100-140 ppm and of carbonyl at 160-180 ppm. MS has the shortest peaks at  $\text{CH}_2$ ,  $\text{CH}_3$  and benzene ring. SB-75 and commercial humic acid look similar in patterns of higher benzene ring content and moderate carbonyl. However, SB-75 has more chain  $\text{CH}_2$ ,  $\text{CH}_3$  structure than the commercial humic acid's. HVC and BB show the outstanding peak at  $\text{CH}_2$ ,  $\text{CH}_3$ . Where as BB has higher benzene ring peak than HVC and also has some peaks of carbonyl. KK has all of the peaks but not as prominent as the others. Thus we can see the significant difference between humic structures of SB-75 and HVC even they came from the same depositional environment.

Fig.6.42 is CP/MAS  $^{13}\text{C}$  NMR of extractable  $\beta$ -humus. This figure shows that HVC has the highest peak at carbonyl and indicates to its humic acid. Nevertheless the conspicuous peaks in this pattern are O-Alkyl cellulose C1-C5 at 70-80 ppm of KK and WN. In addition KK has carbonyl peak and WN has both benzene ring and carbonyl peaks.

### 7.3 Soluble Salts

Table 6.5 shows the soluble salts analysis which are determined of selected ball clay by the Department of Mineral Resources.

The highest soluble sulfate group of ball clays are MS, MVW and BB (above 200 ppm/kg) and follow by MT and HVC (100-200 ppm/kg). The minimum level of soluble sulfate are JK and WN .

In term of  $\text{NO}_3$ , the maximum level are MS, MT (11 and 12 ppm/kg). From view point of soil science; active humic substance is the best chelating agent and have nitrogen at the end of the chain of humic substance. So it will be more active to exchange ions (good Cation Exchange Capacity). MS and MT consist of high  $\text{SO}_4$  and total dissolved solids, thus the N in chelating group dissolved as  $\text{NO}_3$ . Consequently MS and MT yield more chelating agent than the others, which result in lower casting rate. SB-75, HVC, BB are all high in humic substance with more than 40 % is OC which is also high among them. Nevertheless their  $\text{NO}_3$  content are low, consequently, ball clay nitrogen in this part could not dissolve in deionized water. The reason of this may be the fact that the low polarity of deionized water cannot separate NH out of the other content.

The concerning Cations are Ca, Na;

Ca ion is highest in MS, then MVW following by HVC (31 ppm) while SB-75 has a low Ca content. The viscosity studies



reveal that SB-75 has low gelation characteristic. Due to the fact that the narrow double layer in the other clays forms from  $\text{Ca}^{2+}$  ion, in MS and HVC which yield a high gelation property. On the contrary to SB-75, it thick double-layer form from  $\text{Na}^+$  ion.

Na ion is the highest content in SB-75 on the contrary of its low Ca content. Thus it should have the widest double layer; as a result of the low gelation property.

## **7.4 Rheological and Casting Properties**

### **7.4.1 Rheological Properties**

Fig.6.43 shows range of specific gravity that ball clays used in this research can be prepared into ball slips. The specific gravity that made local ball clays into ball slip is in range between 1.55-1.60. Among the local ball clays, the viscosity of MS is the lowest. The imported ball clays can be prepared at specific gravity 1.56-1.70; and reveal at 1.68 the lowest viscosity property of SB-75. The highest viscosity ball clays in this study is JK.

### **Effect of Temperature on Rheology**

Fig.6.44 and 6.45 are showing the effect of temperature on MS and SB-75. They seem to have similar effect of temperature. At  $39^\circ\text{C}$ , MS and SB-75 ball slips both yield the lower viscosity than  $25^\circ\text{C}$  and  $50^\circ\text{C}$ . At  $50^\circ\text{C}$  the viscosity are higher than at  $25^\circ\text{C}$  and  $39^\circ\text{C}$ . This is because water evaporation effect is lower the water content in slip (in opening system test). In this study, the temperature of  $34^\circ\text{C}$  was selected since it is the ball slip preparing process temperature.

## Deflocculation Response

Fig.6.46 shows the inferior deflocculation response of MVW. It yields a narrow curve. The MVW utilizes high amount of  $\text{Na}_2\text{SiO}_3$  (~ 1.00 %) in the process of deflocculation. WN is the clay that used less content of deflocculant at the start of full deflocculation and had very large deflocculation range before flocculated at 1.05 %  $\text{Na}_2\text{SiO}_3$ . Both MS and MT appear similar steep slope but with the different content of  $\text{Na}_2\text{SiO}_3$  which utilized less by MS. This may be the fact that MS has higher soluble sulfate between the two.

Among the group II ball clay, SB-75 use the smallest amount of  $\text{Na}_2\text{SiO}_3$  for full deflocculation. However HVC used twice as much of  $\text{Na}_2\text{SiO}_3$  when compare to SB-75. For HVC has less organic content but use deflocculant less than the others do. BB has less organic content than HVC, consequently BB needs more deflocculant.

In group III (JK, KK, WN, PC), JK has highest viscosity and shorter range of deflocculation. KK has the steep slope till fully deflocculation and shortest range of base line which means easy to flocculation. WN consume smallest of deflocculant in this group and subsequently yield the most declining slope and attain more  $\text{Na}_2\text{SiO}_3$  till fully deflocculation. PC looks similar to WN but utilize more  $\text{Na}_2\text{SiO}_3$  and thus the higher viscosity.

Fig.6.47 shows the effect of adding humic acid to MT ball clay and preparing it into ball slips. They need lesser deflocculant but more or less depending on source of humic as show in this figure. BB humic acid (extracted from BB) utilized the smallest amount of  $\text{Na}_2\text{SiO}_3$ . HVC and commercial humic

acid need more deflocculant than the BB humic acid added ball slip.

Fig.6.48 shows that added different contents of commercial humic acid. At the level of commercial humic acid 0.1 % added ball slip needed the smallest amount of  $\text{Na}_2\text{SiO}_3$ . At the level of 0.3 %, it obviously used deflocculant more than no humic added slip. They showed the effect of humic acid at the deflocculant dosages in an order of the amount added. This might cause by the double layer and steric hindrance effects. When consider the NMR identification, commercial humic acid has the highest amount of benzene ring. When it is used in high content clay particles which will absorb commercial humic acid on their surface. It is due to their chelating agent which prompt to act as cation exchangers and absorb Na ion on humic acid structure (from the model of adsorbed humic on clay particle in Fig.3.11).

### **Gelation and Relative Gel-strength**

Fig.6.49 - 6.51 show the gelation of all ball clays in this study. REX has the lowest viscosity and low gelation property. The highest viscosity belongs to JK but is not a high gelation. MT has viscosity in third order from lowest value but has the highest gelation. The highest viscosity together with gelation come from MVW. MS shows its low viscosity that just only higher than REX's and yields very low gelation (lower than SB-75). SB-75 behaves similar to HVC. BB looks like WN in terms of viscosity and gelation.

Fig 6.52 shows the gelation of MT, which was added different source of humic acid (from commercial humic and extractable humic acid from HVC, BB). We found that when

compare MT that was added 0.1 % commercial humic acid with 0.1 % BB humic acid, their gelation appear similar (lower than MT curve). But adding 0.1 % HVC humic acid ball slip, it show very high gelation so we should expect high casting rate, from Table 6.7 has shown this fact already.

Fig.6.53 presents the effects of adding different contents of commercial humic acid to MT ball slips. MT ball slip seems to have very high gelation compare with added commercial humic acid ball slips. At the level of adding 0.1 % MT slip show lowest viscosity and gelation Whereas at 0.2 and 0.3 % level added of commercial humic acid added has higher gelation than at 0.1 % does. The amount of sodium silicate used with different dosages of humic acid seems to be higher when adding more content of humic acid. It can be explained this commercial humic acid used though in this research is the humic product prepared for agriculture purpose, which consists of high chelating agent, or very active humic acid (for most CEC). So it likes to absorb more cations on its structure.

Fig.6.54 indicate the relative gel-strength of ball slip. It obviously presents the highest gelation and viscosity after gel left. It is very high in MT ball slip that conforms to gelation in Fig.6.49. MS, SB-75, HVC, REX and BB behave the same way after gel period, the viscosity is lower when we start to rotate the spindle hence this show trend of good drain.

JK and KK have straight line of viscosity after break gel. This indicates not a good response to shear force of ball slip. The most inferior in this study is MVW.

The interesting results from Fig.6.55 are MT added with 0.1 % HVC extractable humic acid. It is showing the

highest gelation and high viscosity after break gel. However, the 0.1 % commercial humic acid added ball slip and 0.1 % BB humic acid added ball slips behave similar way for low gel, so that curves after gel period flatter than unadded MT.

The curve rank in Fig.6.56 has confirmed Fig.6.53 in term of effect of adding humic acid. The lowest gelation is 0.1 % commercial humic acid. It show outstanding effect of commercial humic content in the picture that the higher humic content, the higher shear response after gel period. The highest shear response in this case is at the 0.3 % commercial humic acid added slip.

### **Shear Response**

Fig.6.57 through 6.78 show shear rate-shear stress curves of all ball clay samples. They depict pseudoplastic thixotropic curves except for MVW (Fig.6.59), MT added 0.1 % HVC humic acid (Fig.6.81) and 0.1 % commercial humic acid (Fig.6.85) show dilatant curves. It can be explained by theory of deflocculation and protective colloids in chapter 3 that fully deflocculation slip gives dilatant flow at high shear rate. Shear rate-viscosity curves of all samples show the same effect that high shear rate course lowering viscosity but the sensitivity depending on which clay. Fig.6.82 show large loop of shear rate-viscosity curve, it causes by the gelation effect of its high gelation of slip contained HVC humic acid which also show dilatant curve when sheared at high shear rate.

Shear response in term of shear rate-viscosity curve are presented in Fig.6.58, 6.60, 6.62, 6.64, 6.66, 6.68, 6.70, 6.72, 6.74, 6.76, 6.78 and 6.80 from ball clay samples. For humic acid added MT test are shown in Fig.6.82, 6.84, 6.86,

6.88 and 6.90. Fig.6.58 of MS shows time dependent thixotropic effect. Fig.6.60(MVW) and 6.62(MT) show high effect of expected high gelation. Fig.6.64(SB-75), 6.66(HVC), 6.68(REX) and 6.70(BB) show the superimpose of increasing and decreasing shear rate and they behave all in the same manner. Fig.6.72(JK), 6.74(KK), 6.76(WN) and 6.78(PC) show the same response on shear rate similar to those in group II ball clays.

When adding humic acid from commercial purpose and extractable humic acid of some ball clay samples we have seen from Fig.6.82(0.1 % HVC humic acid), Fig.6.84(0.1 % BB humic acid), Fig.6.86(0.1 % commercial humic acid), Fig.6.88 (0.2 % commercial humic acid) and Fig.6.90(0.3 % commercial humic acid). They all show the change from the original MT slip that has been narrow loop to superimpose of increasing and decreasing shear rate except only by adding 0.1 % HVC humic acid in Fig.6.82 which is high gelation.

#### 7.4.2 Casting Properties

Table 6.6 shows the casting properties of ball clay samples. The highest casting rate ball clay in this study is MT which is conformed to its highest gelation. In group I, MS is the lowest casting rate but MT has the contrast of thixo at 1 min., it has same thixotropy as MS but yield nearly triple casting rate. KK is the highest thixotropy at 1 min. when compare among the local ball clays group which have been prepared at the same specific gravity (1.55 gm/ml). For group II ball clay, BB is the highest thixotropy at 1 min. without any difference from the others in the casting rate. In term of permeability of ball clay cake, MT has most filtrate weight. Group III ball clays have the same values of filtrate weight about 4 gm. Table 6.7 illustrates this property changes when

added different source of humic acid in the same amount. We found that cast rate 30 min. and Baroid cake weight will decrease when added humic acid except only at 0.1 % HVC humic acid added. This resulted in high gelation. HVC dominates its properties of low viscosity, high gelation, which yield high casting rate. Consequently, this can be resulted from HVC's humic acid structure, which consists in form of chains rather than rings. Thus it appears the effect of sphere influence will create more bonding between gelation.

Table 6.8 MT added different content of commercial humic acid, from 0.1-0.3 %, casting rate and Baroid cake weight will decrease corresponding to the increase contents of humic acid.



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