Diagnostic evaluation of bentonitic and kaolinitic clayey materials for ceramic applications

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ABSTRACT

Samples of bentonitic and kaolinitic clayey materials obtained from clay occurrences and deposits from around the world were diagnostically evaluated for their suitability for use in the ceramic industry. Evaluative tests were Atterberg limits (liquid limit, LL; plastic limit, PL; and plasticity index, PI), linear and volume shrinkage, and organic matter contents. Values obtained for LL ranged from 22.4 to 390 %; for PL were from 24.1 to 86.8 %; and for PI the figures were from 13 to 252.5 %. Linear shrinkage values were from 2.5 to 30 wt %, and volume shrinkage figures were from -32 to 17.6 %. Total organic carbon (TOC) contents were from 0.31 to 1.34 wt %. Samples with low plasticity also had low shrinkage and low organic content; and these were identified as kaolinitic clayey materials, whereas samples with high plasticity, high shrinkage and high organic content were bentonitic clayey materials. The results depict that increase in clay plasticity has a direct bearing on shrinkage and organic matter. Clay workability favour the use of the kaolinitic clay in ceramics. However, the bentonitic clays could be utilized as additives in increasing the plasticity of some of the kaolinitic clays with very low plasticity. Other related beneficiation tests may have to be carried out for tailor made applications of the studied clayey materials in the ceramic industry.

Key words: Clay, liquid limit, plastic limit, plastic index, shrinkage, total organic matter

RÉSUME

Des matériaux argileux bentonitiques et kaolinitiques des différentes sources de part le monde ont été soumis a une évaluation diagnostique pour leur suitabilité dans l'industrie céramique. L'évaluation comprenait les tests suivants : limites Atterberg (limite liquide, LL ; limite plastique, LP ; et l'indice de plasticité, IP), rétrécissement volumique et linéaire, et la détermination du contenu organique. La limite liquide présentait des valeurs s'étalant entre 22.4 et 390% ; pendant que la limite plastique s'étalait entre 24.1et 86.8%, et l'indice de plasticité était entre 13 et 252.5%. Le rétrécissement linéaire et volumique s'étalaient respectivement entre 2.5 et 50 % en poids pour l'un et entre -32 et 17.6 % pour l'autre. Le contenu total en carbone organique (TCO) s'étalait entre 0.31 et 1.34% en poids. Les résultats expérimentaux montrent que les échantillons à faible plasticité présentaient aussi une faible teneur en contenu organique. Ils étaient ainsi identifiés comme matériaux argileux kaolinitiques pendant que les échantillons a plasticité élevée, a grand rétrécissement et haute teneur en contenu organique étaient identifiés comme des matériaux argileux bentonitiques. Des résultats obtenus il s'avère que l'argile kaolinitique s'apprête à des applications céramiques. Les argiles bentonitiques s'utiliseraient mieux comme additifs pour l'augmentation de la plasticité des argiles kaolinitiques a faible plasticité. L'étude ci-dessus montre que des traitements et enrichissements appropriés des matériaux argileux utilisés seraient recommandés pour leurs applications spécifiques dans l'industrie céramique.

Mots cles: argile, limite liquide, limite plastique, indice de plasticité, rétréceissement, contenu total en carbon organique

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INTRODUCTION

Ceramic production has remained the principal consumer of ball clays (of which the main mineral is kaolinite) and plastic clays throughout the world (Stentiford, 1996). Innovations in the consumption market of clays and clay minerals including bentonites and kaolins, have made raw materials suppliers to direct their production to meet with changing demands of customers (Bertrand, 1996). In the ceramic industry, kaolin is used in four areas: refractories, sanitaryware, floor tiles, and dinnerware & pottery (Bertrand, 1996); and it also finds application in the production of glazes. It produces white color at a profitable price, and regulates slip rheological properties and casting thickness in claybodies. It also contributes to stability and adherence of slips and glazes (Stentiford, 1996). Bentonites have a number of commercial uses, which are directly related to their absorptive, plastic and swelling properties that are equally employed in the ceramic industry.

The plasticity of clay is a measure of the ease with which the clay body can be formed/molded into different shapes. The workability of any clayey material is the degree to which it can be manipulated in order to obtain the desired product. Plasticity is the property that allows a claybody to be deformed under stress and retain its shape even after the stress has been removed, without rupture of the body (Ramonyane, 1986). This property is very important in the ceramic industry where the raw claybody has to be worked to the desired shape. Low plasticity kaolinitic mudstones have been found to have low to moderate drying shrinkage and poor workability which can be improved by the addition of bentonite (Ramonyane, 1986). In such a case, bentonite is added to kaolinite in order to enhance the plasticity and strength of the formulated claybody.

The Plasticity Index (PI) of bentonite is directly related to the amounts and types of minerals present, as well as orientation and size of clay particles. When dispersed in water, montmorillonite exhibits strong plasticity and stickiness in a wet state (Tan, 1998). Dry swelling bentonites have a higher PI than dry non-swelling bentonites. White bentonite is used as plasticisers in ceramics, particularly in porcelain bodies. Its high water absorption and water retention properties makes it effective in sufficiently small amounts without compromising shrinkage on firing (Ciullo, 1996). In the production of whiteware, electrical porcelain and technical ceramics, white bentonite clay products are used for greater control of body plasticity in order to minimize reject rates (Clarke, 1982). It is an additive used to enhance production, improve green strength, and increase water resistance and boost yield.

During manufacturing, claybodies shrink due to the removal of interparticle water as they dry. Fine particle-sized clays with high plasticity such as montmorillonite have high shrinkage, which is a disadvantage in the ceramic industry. Shrinkage may not be used as an indicator of plasticity because not all fine clays have high plasticity. Clays can shrink as little as 4 % and as much as 25 %, and in ceramics, a shrinkage value of 12 % is acceptable (Parras *et. al.*, 1996). Dry shrinkage for non-plastic clays is below 7 %; while for plastic clays the value is higher. Ceramic claybodies of Ordovician Shales (which are the hostrock of the clays), from Spain have linear shrinkage of < 8 % (Parras *et. al.*, 1996). Composite claybodies have shrinkage values, which are different from the values of individual clay minerals. High shrinkage can be removed by adding aggregates which produce a matrix having macro-cracks radiating outward from each other, with a weak dried finished product of high fragility. A low drying shrinkage is suitable for drying larger wares of uneven cross section.

It is important to have an idea of the organic matter contained in a claybody before firing. Firing starts after atmospheric drying of the claybody where heating should be slowly done. Organics need to be burnt out, and this must be achieved under very favorable oxidizing conditions; or else the color of the finished product may be darkened.

Because bentonitic and kaolinitic clayey materials occur worldwide and are well employed in the ceramic industry, there was need to appraise the performances of some of these materials currently not employed in the ceramic industry, and advise on their suitability for use therein, based on the outcome of this study. Therefore diagnostic evaluative tests were performed on bentonite and kaolin samples to evaluate their suitability for use in the ceramic industry. The conducted analyses included Atterberg Limits tests {Plastic limit (PL), Liquid limit (LL), and plasticity index (PI)}, Shrinkage tests (linear and volumetric shrinkages), and organic matter determination.

Table 1: Mineralogy of raw clay samples as determined by X – ray diffraction study

Sample	Chlorite	Montmor	Beidellite	Nontroni	Illite-mont	Lepidolit	kaolinite	Dickite	Nacrite	Pyrophyl lite	Muscovit	Illite	Cristobal	Cordierit	Augite	Calcite	Quartz	Microclin	Ilmenite
1		√	√										√				√		
2		√			√								√				√		
3		√														√	√		
4		√	√													√	√		
5	√			√							√		√	√			√	√	
6	√											√	√				√		
7	√	√			√							√		√			√		√
8	√						√								√		√		
9	√						√										√	√	
10	√	√					√			√		√					√		
11							√	√				√					√		
12							√	√		√	√	√					√		
13						√	√					√					√		
14		√				√		√		√		√					√		
15	√	√							√	√		√					√		
16		√					√										√		
17							√				√						√		

EXPERIMENTAL

Samples of clayey materials

The 17 samples of clayey materials analysed in this study were obtained from clay occurrences and deposits in Botswana, Mozambique, Pakistan, Senegal, South Africa, and United States of America (USA). In a separate study by Ekosse *et. al.* (2004), the mineralogy of the clay samples were determined, and are hereby given in Table 1 as the basis to work with. Samples of clayey materials consisted of either smectite or kaolinite as the major clay mineral phase contained in them, as well as other related clay mineral assemblages.

Atterberg limits tests

The tests performed were the liquid limit (LL) and plastic limit (PL). The LL technique employed was the cone penetrometer (BS 1377, test 2A, 1975), and PL technique used was the BS 1377, test 3 (1975). The difference between the LL and PL was calculated to give the plasticity index of the sample as stated in equation (1).

$$PI = LL - PL \qquad (1)$$

Shrinkage tests

Two types of shrinkage tests were performed on the samples: volumetric shrinkage and linear shrinkage. The technique used for volumetric shrinkage measurement is the American Standard of Testing Materials (ASTM) test, which is described in the United States Bureau of Roads Earth Manual in the section, "Test Designation E-7, Part C" (USBR, 1990). The technique used in determining the linear shrinkage of clay samples was that of the BS 1377 of 1975, test 5.

Determination of organic matter

Samples were analyzed quantitatively for their total organic carbon (TOC) contents using a LECO RC-412 multiphase Carbon/Hydrogen/Moisture Determinator. The principle is based on converting all C to CO_2 in an oxidizing analytical atmosphere. The organic form of C produces both H_2O and CO_2, which enables TOC to be measured from observable H_2O peaks. The quantitative analysis program was set for the time and temperature required, which is thirty minutes at 125 °C, after qualitative tests were conducted to obtain the ranges.

RESULTS

Atterberg limits tests

The results of the Atterberg limits and shrinkage tests are given in Table 2. Atterberg limits tests were not performed on samples 6, 7, 8, 9 and 15 because

Table 2: Liquid limit, plastic limit, plasticity index, linear shrinkage and volume shrinkage of samples

Sample No	Liquid limit	Plastic limit	Plasticity index	Shrinkage (%)	
				Linear	Volume
MT1	188	66.8	121.2	27.1	-32
MT2	344	81.8	252.5	29	-24
MT3	230	72.4	157.6	28.3	-17
MT4	390	86.8	303.2	30	-20
MT5	22.4	Non plastic	Non plastic	Non plastic	Non plastic
MT10	37.4	24.4	13	5	14.9
MT11	45.4	24.6	20.8	5.8	14.5
MT12	43.6	24.2	19.4	5.9	8.5
MT13	54.3	24.1	30.1	6	8.4
MT14	44.4	29.7	14.7	5.8	17.6
MT16	44.5	25.0	19.5	2.5	4.5
MT17	50	28	22	4	6

the quantities were very small. Values obtained for liquid limit (LL) of clay samples ranged from 22.4 % for sample 4 to 390 % for sample 2. Values also obtained for plastic limit (PL), ranged from 24.1 % for sample 13 to 86.8 % for sample 4. Sample 5 was determined as non-plastic material. It was observed that smectitic clay samples had both higher LL and PL than kaolinitic clay samples as depicted in Figure 1.

Based on both LL and PL, the samples could be grouped into two classes. The first class was samples with LL and PL values exceeding 100 % and 40 % respectively; and these were samples 1, 2, 3 and 4. The second class was samples with LL and PL values below 100 % and about 40 % respectively; and these were samples 10, 11, 12, 13, 14, 16 and 17. These two classes were reflected from the plot of LL against PL (Figure 1). A similar trend of distribution of samples was observed for a correlation of plastic limit (PL) and plasticity index (PI) as shown in Figure 2. This trend confirmed that samples 1 to 4 are more plastic than the other samples. The PI values obtained for clay samples ranged from 13 % for sample 10 to 252.5 % for sample 2. Sample 5 was determined as non plastic. The clays were grouped into two based on their PI values. The first group of samples comprised those with

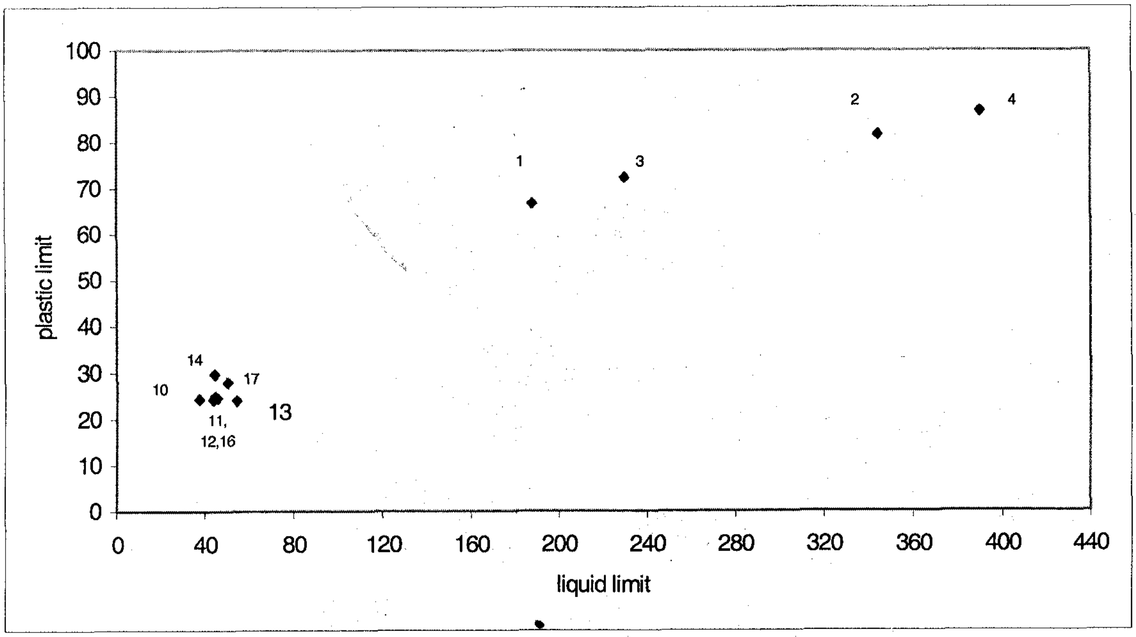

Figure 1: Correlation of plastic limit and liquid limit of clayey materials (sample numbers are indicated in the graph)

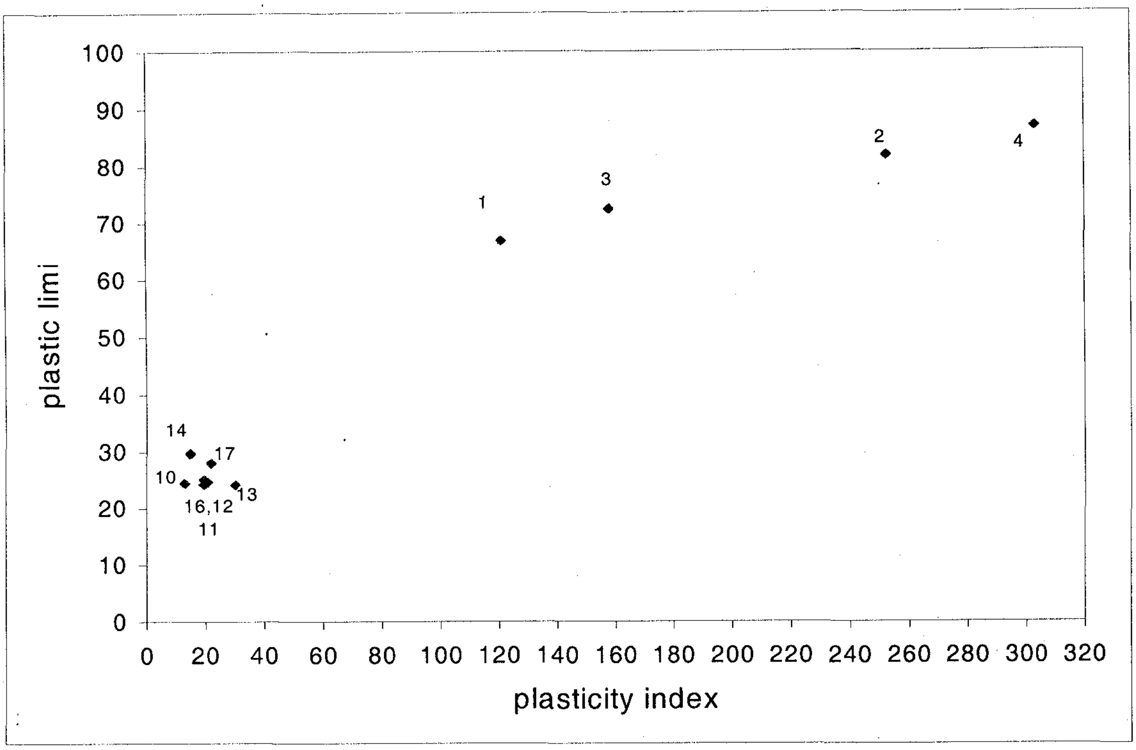

Figure 2: Correlation of plastic limit and plasticity index of clayey materials (sample numbers are indicated in the graph)

very high PI values exceeding 40 %, and these were samples 1. 2, 3 and 4. The second group of samples were those with PI values below 40 %, and these were samples 10, 11, 12, 13, 14, 16 and 17.

Shrinkage tests

Shrinkage tests could not be performed on samples 6, 7, 8, and 9 because the quantities were very small. Sample 5 was a non - plastic material. A correlation diagram of the volume shrinkage versus the linear shrinkage is given in Figure 3. From the scatter plot diagram, the clay samples were distinctly discriminatory, and they could be classified into two clear-cut groups. The first group was reflective of smectitic samples with high linear shrinkage values of between 25 and 30 %. The second group was

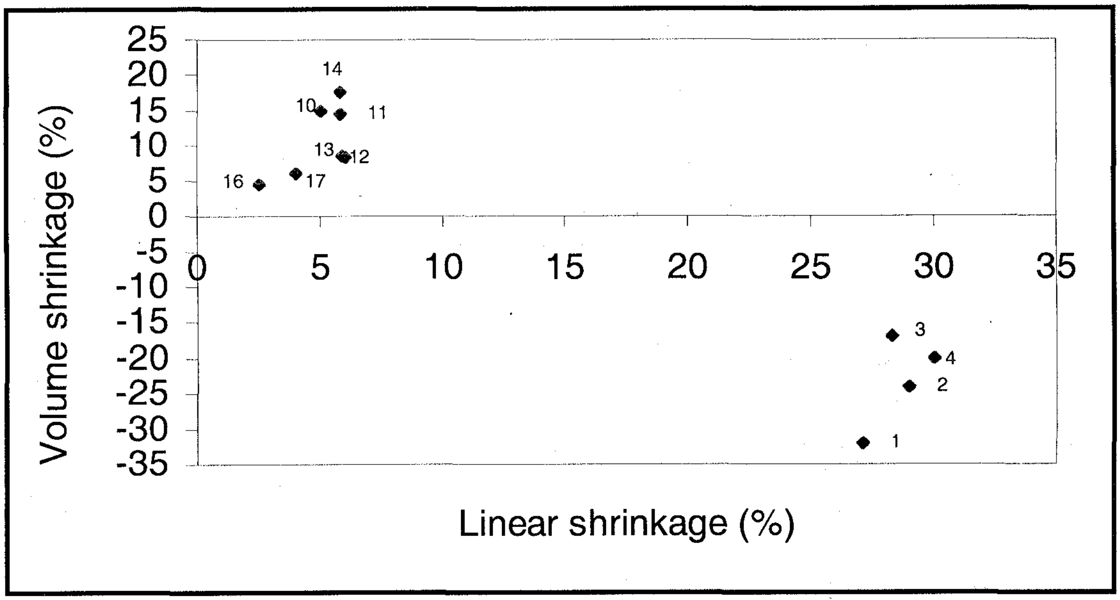

Figure 3: Correlation diagram of volume shrinkage and linear shrinkage values for clayey materials (sample numbers are indicated in the graph)

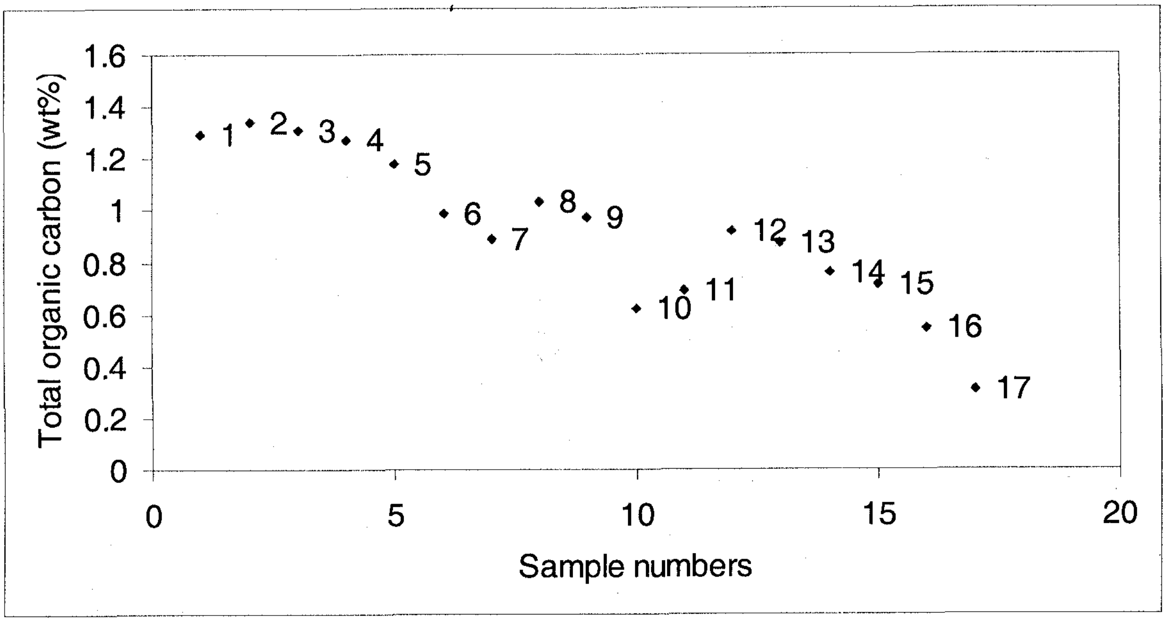

Figure 4: Total organic carbon (TOC) content of clayey materials (sample numbers are indicated in the graph)

indicative of kaolinitic samples having low linear shrinkage values between 2.5 and 7 %.

From Figure 3, it is evident that the linear and volume shrinkage values for the smectitic samples were higher than the values obtained for the kaolinitic samples. Sample 16 had the lowest value for linear shrinkage, which was 2.5 % and sample 4 had the highest which was 30 %. Sample 1 had the lowest value of volume shrinkage, which was -32 % and sample 14, the highest being 17.6 %.

Total organic carbon

Total organic carbon content varied from 0.31 to 1.34 wt %, with the bentonitic clays having the higher values compared to the kaolinitic clays (Figure 4). The trend is in conformity with clay mineral formation and deposition. Bentonites in general have higher organic matter content compared to kaolins.

DISCUSSIONS

Aspects of Atterberg limits values

Clay plasticity is a very important parameter, which assists in determining the application of a given claybody. Clay plasticity is the property, which enables the ease of manipulation and/or workability of a given clayey material. Increase in clay plasticity is directly proportional to increase in shrinkage. Bentonites are known to have very high plasticity compared to other clays including kaolins. The studied clay samples were plotted using the clay workability chart according to Bain and Highley (1978), and presented in Figure 5. Bain and Highley (1978) formulated a clay workability chart, which is recognized in the use of clayey materials. Samples 10, 14 and 17 had acceptable molding properties. Samples 11, 12, 13, and 16 manifested optimum molding properties. Sample 13 was found to be very suitable for the making of pottery vessels. Samples 1, 2, 3 and 4 were outliers within the classification scheme of Bain and Highley (1978), but if they could be blended with clays of very low plasticity, they could be conveniently utilized in brick making and pottery.

Normal plasticity index for ceramic clays is about 30-35 (Konta, 1980). In general, the bentonitic clays being highly more plastic and out of the range for use in ceramics than the kaolinitic clays, need to be blended with kaolinitic and/or chloritic clays subsequent to their usage in the ceramic industry. Even more reasonable, they should be used as value-added clays to augment plasticity of claybodies, which are deprived of montmorillonite. Other previous studies carried out by Ekosse (2000), Christidis and Scott (1997), Dondi *et. al.* (1992), and Cravero *et. al.* (2000) support these recommendations for the studied clays.

Clays of high plasticity, and more specifically bentonite, are very difficult to mine using small-scale mining techniques because when wet, they are very elastic and rubber-like to dig through and when

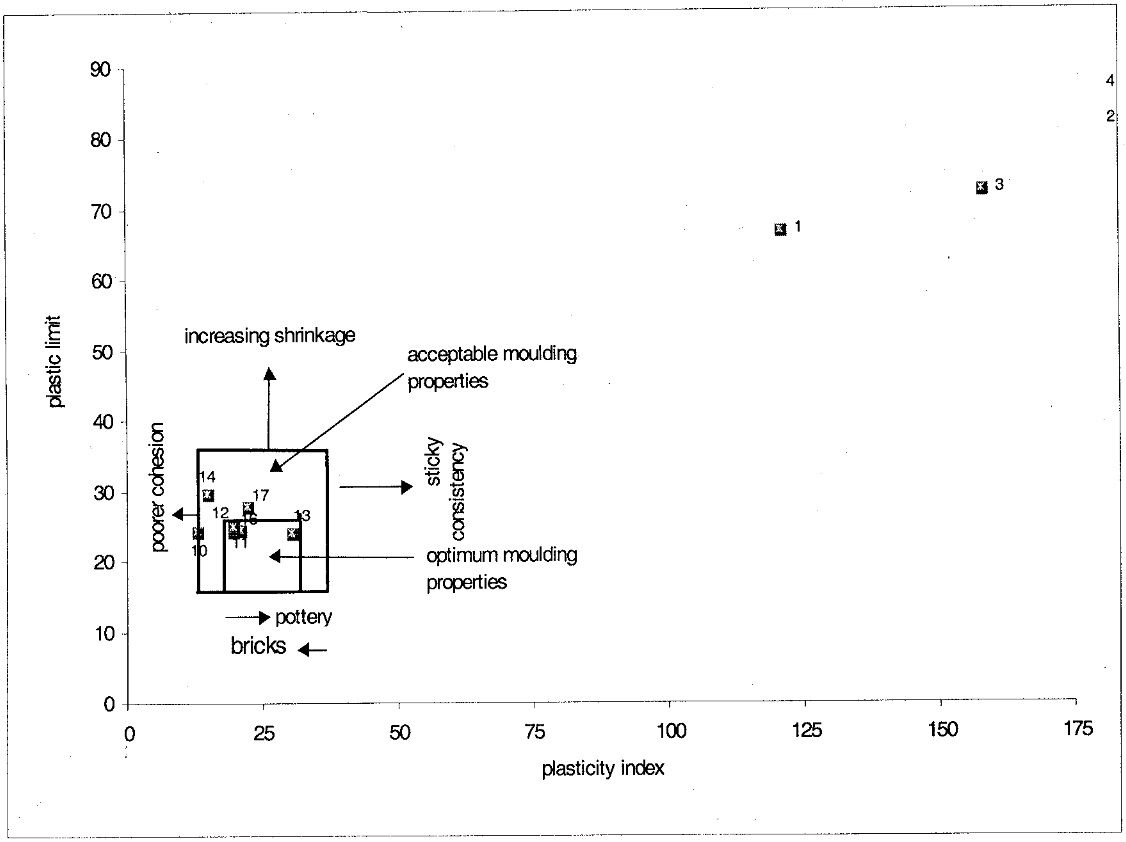

Figure 5: Clay workability chart (after Bain and Highley, 1978). (Numbers are indicative of sample numbers and are preceded by MT)

dry, they are very hard, almost impervious except for cracks, exfoliated surfaces and peel-offs. Clays of low plasticity and especially kaolins, on the other hand, are easily mined because they are soft and easily penetrated. In the past, they were mined in ball-like chunks, hence being named ball clays.

Aspects of organic matter

Organic matter in clays is reflected analytically by the amount of organic carbon contained in the clay sample. Carbonaceous matter present in clays contributes to the plasticity of the claybody. Organic matter in small amounts helps to develop clay plasticity, but when it is too much, causes clay stickiness and high shrinkage (Plasticity and origin of clays, 2001).

High organic matter in clay affects the color and structure of the finished product. Organics in claybodies need to be burnt out, and this is achieved under very favorable oxidizing conditions. The release of organic gases at low temperatures may cause blistering on the claybody. Due to the fact that the organic carbon content in the studied clay samples were considerably low, organic matter may not pose as an obstacle in the use of the clayey materials for ceramics.

Aspects of shrinkage

Fired shrinkage is characterized by the breaking down, reacting, melting and flowing of claybodies to more stable forms and colour changes because of the application of heat (Ekosse *et al.*, 2003). As claybodies were fired, they shrank and particles continued to collect together in a closely knitted manner. Eventually, there was breaking down and reaction of the particles with each other. Particles started to flux together, melt and flow, as temperature increased in the reaction medium (Galan *et. al.*, 1996). The mineral grains seeded the development and production of more stable forms of minerals. The degree of shrinkage during firing is an indication of the degree to which the complex maturing process has proceeded (Physics of claybodies, 2000).

The values obtained for shrinkage tests for the studied samples were clearly divided into two groups. Samples 10, 11, 12, 13, 14, 15, 16 and 17 had acceptable linear shrinkage values (between 2.5 and 7 %), and volume shrinkage values (between 5 and 17.6 %). These values are acceptable, and even up to 12 % in ceramic industries (Parras *et. al.*, 1996). Other researchers (Galan *et. al.*, 1996; Ligas *et. al.*, 1997;

and Dondi, 1999), obtained similar values and recommended their researched clays to be suitable for use in the ceramic industry. The second group of clay samples were samples 1, 2, 3 and 4 that had linear shrinkage values (between 25 and 30 %), and volume shrinkage values (between -15 and – 32 %). These values were found to be higher than the acceptable ones utilized in the ceramic industry. Consequently, the clays must be blended with clays of lower shrinkage values to obtain an acceptable range for ceramic applications.

CONCLUSIONS

In this study, investigations on the Atterberg Limits tests (PL, LL and PI), shrinkage tests (linear and volumetric shrinkages), and organic matter content were carried out on 17 different clayey samples obtained from around the world in order to investigate their suitability for use in the ceramic industry. Results depict that some of the clayey materials behave as bentonitic clays and others as kaolinitic clays. The bentonitic clayey materials had high plasticity, high shrinkage and high organic content, and the reverse was applicable for the kaolinitic clayey material.

Based on clay workability, the kaolinitic clayey materials could be gainfully utilised in ceramics. Regarding the bentonitic clays, they could be employed as additives in increasing the plasticity of some of the kaolinitic clays with very low plasticity. However, a need for related beneficiation tests may have to be carried before engaging the studied clays for tailor made applications.

REFERENCES

Bain J. A. and Highley D.E. (1978) Regional appraisal of clay resources challenge to the clay mineralogist. In: M. M. Mortland and V. C. Faxmer (Editors), Proc. Int. Clay Conf. Elsevier, Amsterdam, pp437-446

Bertrand T. (1996) Kaolin in ceramics - A view from Europe. 65-67. In Kendall T. Editor. Industrial clays. 2nd edition. *Industrial Minerals.* 78 pages

BS 1377 test 2A (1975) British Standards for the determination of the liquid limit of soils. *Liquid and Plastic Limits.* Pp 69-73

BS 1377 test 3 (1975) British Standards for the determination of the plastic limit of soils. *Liquid and Plastic Limits.* Pp 73-76

BS 1377 test 3 (1975) British Standards for the determination of the plastic limit of soils. *Shrinkage tests.* Pp 101-117

Christidis G. and Scott P (1997) The origin and control of colour of white bentonites from Aegean islands of Milos and Kimolos, Greece. *Mineralium deposita.* **32**, 271-279

Ciullo P.A. (1996) White bentonite A bright future 18-22. In Kendall T. Editor. *Industrial clays.* 2nd edition. Industrial Minerals. 78 pp.

Clarke G. (1982) Bentonite - a review of world production. *Industrial Minerals* October 1982 23-43

Cravero F., Keith K. S., Murray H. H., Toth T. (2000) A white bentonite from San Juan Province, Argentina - geology and potential industrial applications. *Applied Clay Science* 16, 31-43

Dondi M., Fabbri B. and Laviano R. (1992) Characteristics of the clays utilized in the brick industry in Apulia and Basilicata (southern Italy). *Miner. Petrogr. Acta.* **35**, 181-191

Ekosse G. (2000) The Makoro kaolin deposit, southeastern Botswana: its genesis and possible industrial applications. *Applied Clay Science* **16**, 301-320

Ekosse G. (2001) Provenance of the Kgwakgwe kaolin deposit in south eastern Botswana and its possible utilization. *Applied Clay Science.* **20**, 137-152

Ekosse G., Mulaba A. F., and Nkoma J.S. (2003) Effect of firing on color of clayey materials applied to traditional ceramics. *Botswana Journal of Technology* **12**, 13-18

Ekosse G., Mulaba-Bafubiandi A. F. and Nkoma J. S. (2005) Vitrification and neomineralization of bentonitic and kaolinitic clays for possible ceramic applications. *Global Journal of Geological Sciences* **3** (2) 153-161.

Galan E., Aparicio P., Miras A., Michailidis K. and Tsirambides A. (1996) Technical properties of compounded kaolin sample from Griva (Macedonia, Greece). *Applied Clay Science.* **10**, 477-490

Konta J. (1980) Properties of ceramic raw materials. Ceramic monographs. Handbook of ceramics. Schmid Frieburg, pp 1-32

Ligas P., Uras I., Dondi M., and Marsigli M. (1997) Kaolinitic materials from Romana (north-west Sardina, Italy) and their ceramic properties. *Applied Clay Science* **12**, 145-163

Parras J., Sanchez-Jimenez C., Rodas M., and Luque F.J. (1996) Ceramic applications of Middle Ordivician shales from central Spain. *Applied Clay Science* **11**, 25-41.

Physics of claybodies (2000) The Physics of claybodies. File:///A/physicsofclay.htm. 8pp

Plasticity and origin of clays (2001) Plasticity and the origin of clays. http://www.hamgil.com/Plasticity.html. 4 pages

Ramonyane P. (1986) Assessment of the Foley kaolinitic mudstone deposit for clay based refractories and vitreous ceramic claywares. *Unpublished MSc thesis.* University of Hull, Britain. 131 pages

Stentiford M.J.(1996) Ball clays. Demand strong, but shifting. 39-44. In Kendall T. Editor. Industrial clays. 2nd edition. *Industrial Minerals.* 78 pages

Tan K. H. (1998) Principles of soil chemistry. Mariel Dekker Inc. USA. 521 pages.

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