Asian Journal of Chemistry Vol. 18, No. 2 (2006), 1352–1360

Duvertepe Kaolin Deposits in Balikesir (North-west Turkey) and Ceramic Properties

AHMET MAHMUT KILIÇ, OZEN KILIÇ* and A. EKREM ARITAN†
Mining Engineering Department, Cukurova University, 01330 Adana, Turkey
Fax: (90)(322)3386126; Tel: (90)(322)3386503
E-mail: zenkilic@cu.edu.tr

The Duvertepe kaolin deposits (Caltilitaban and Bagkiran) were characterized and assessed potentially in the ceramic industry. The particle size, colour measurement, viscosity, plastic limits, liquid limits, firing shrinkage, water absorption, water-soluble matter and moisture were tested by chemical, physico-mechanical, mineralogical and the thermal analysis techniques (TG-DTA) and their firing behaviours were investigated. The technological properties of Duvertepe kaolins were determined concerning shrinkage, firing and colour. From these studies, it was understood that the Duvertepe kaolin could be used for ceramic industry, fabrication of tiles, bricks and sanitary wares.

Key Words: Kaolin evaluation, Ceramic, Duvertepe, Technological properties.

INTRODUCTION

Kaolinite is one of the most important clay minerals occurring in large amounts in sediments and sedimentary rocks or as alteration product in crystalline rocks. Because of widespread occurrence and its physical and chemical properties, kaolinite is widely used in certain technical applications regarding physical, chemical, mineralogical properties and thermal behaviour, e.g., ceramic industry, filling material and refractory materials[1–5].

This study deals with the chemical-mineralogical characterization and the technological properties of kaolins from Duvertepe (Balikesir, Turkey). Several kaolin mineralizations occur in this district. The deposits of this area have a high economic potentiality and thus a study of the ceramic properties has been carried out. The reserves of kaolinitic materials have been estimated to amount to 70 million tons[6].

The relationship between the technological characteristics and the mineralogical and chemical features were investigated. The influences of some minor elements (iron, magnesium and sulphur) on the ceramic properties of final products were also taken into account. The comparison between chemical-min-

---

†Mining Engineering Department, Afyon Kocatepe University, Afyon, Turkey.

eralogical and technological properties of the Duvertepe kaolins with other kaolinitic products available on the Turkish market has allowed to define the possible industrial uses of these materials.

The present study provides the evaluation of physical properties of the Duvertepe kaolin deposits and their suitability for use in ceramic industry. These products are then assessed with respect to established specifications and their potential for industrial use. The results of laboratory research of chemical, physico-chemical, mineralogical and thermal analysis techniques of kaolinite ore from the Duvertepe deposit (Caltilitaban and Bagkiran) are presented in this paper.

EXPERIMENTAL

Kaolin samples were taken from two different regions (Caltilitaban, K_C, and Bagkiran, K_B) of Duvertepe deposit. In order to assess the chemical, mineralogical compositions, specific physical and technological properties of representative bulk samples of kaolin have been studied. The physical properties evaluated are: particle size analysis, colour measurement, plastic-liquid limit, differential thermal and thermogravimetric analyses, drying and firing shrinkages and water absorption. Sampling was based on the assumption that materials having different chemical and mineralogical composition would also have different physico-chemical and technological properties. Therefore preliminary chemical and mineralogical analyses have been carried out.

XRF (Siemens SRS 300 X-ray fluorescence spectrometer) was used to determine the chemical compositions of kaolin samples. The loss on ignition was determined by heating at 900°C for 2 h. Mineralogical analyses were carried out by Shimadzu XRD-6000 and Cu X-ray tube ($\lambda = 1.5405$ Å). The diffraction interval was between 2θ–20°–60° with a step of 0.02°. Atterberg limits were determined using the procedure of British Standard BS-1377[7]. Differential thermal and thermogravimetric analyses were carried out to determine the various compounds present in the sample quantitatively and qualitatively. Analyses were performed in samples of kaolin in nitrogen atmosphere with Pt thermocouple at a temperature range of 25–1100°C and a gradient of 10°C/min (simultaneous TG/DTA; Setaram 9216 DTA-TG). Calcined Al_2O_3 served as the inert standard. Colour measurement was performed by the reflected light colorimeter, by green light, model of Canadian Research Institute CG-186. Drying and firing shrinkage was determined by the method of Murray[8]. Water absorption values of Duvertepe kaolin were determined by the routine procedure involving boiling a previously prepared and fired briquette in a beaker of water and measuring the amount absorbed.

RESULTS AND DISCUSSION

The properties determined from samples of the Duvertepe kaolin are described below and evaluated by comparisons with the limits.

Chemical and mineralogical analyses

Table-1 shows the chemical compositions of the Duvertepe kaolin samples (Caltilitaban, K_C, and Bagkiran, K_B). The samples have SiO_2 contents ranging from 49–68% and Al_2O_3 contents ranging from 21–33% (Table-1). Alkaline and alkaline-earth metal and magnesium content are fairly low (less than 1%). MgO may be attributed to the presence of altered femic minerals (hornblende?) that cannot be detected by diffractometric technique. Similarly, the Na_2O content (*ca.* 0.15%) probably depends on the presence of minor amounts of residual feldspar, scarcely altered and not detectable by XRD. Percentages of Fe_2O_3 are sometimes detected; they may be ascribed mainly to the presence of hematite, which was actually detected by XRD.

TABLE-1
CHEMICAL COMPOSITIONS OF KAOLIN SAMPLES

Sample	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	Na_2O	K_2O	SO_3	CaO	MgO	BaO	L.O.I.
K_C	68.85	21.16	0.31	0.50	0.16	0.04	1.11	0.03	0.03	0.00	7.81
K_B	49.31	33.18	0.45	0.20	0.15	1.03	4.75	0.09	0.06	0.11	10.52

L.O.I. = Loss on ignition.

The mineralogical composition of K_C and K_B kaolinite samples mineralogical analysis depicted that kaolin is composed of quartz, muscovite, goethite, alunite, ilmenite and rutile minerals (Fig. 1). X-ray diffraction analysis of these samples fortified that kaolin is the dominant mineral and coexists with quartz.

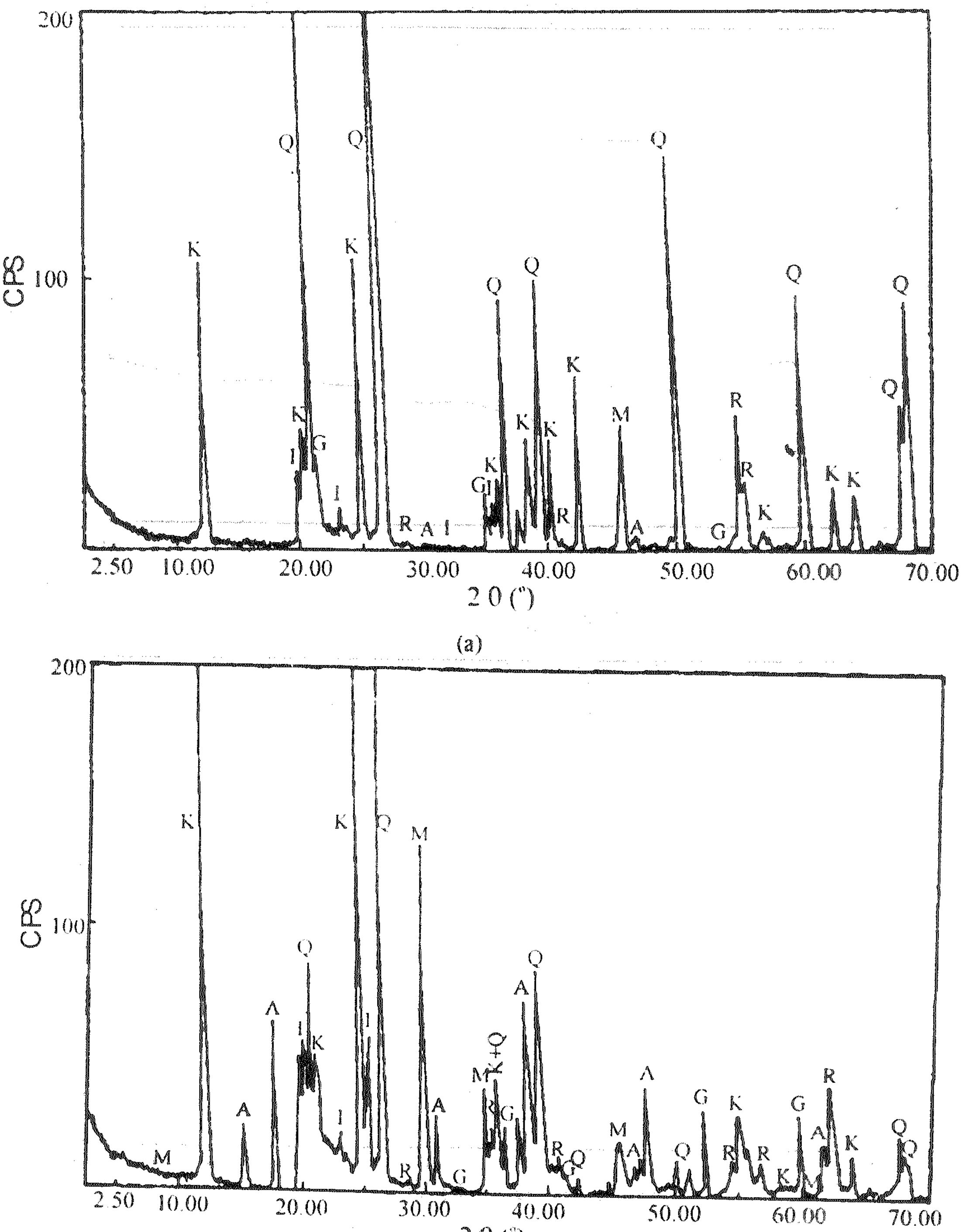
Particle size analysis

The particle size and size distribution are the key factors for the industrial uses of kaolin. Coarse-particle clays differ from fine-particle clays in certain other physical and optical properties as well[9, 10]. The particle size distribution also controls brightness, slurry-viscosity, opacity, gloss, ceramic strength, shrinkage and the paper-filling and paper-coating properties such as the mechanical, optical and printing characteristics of paper sheets[11]. The results of particle-size analysis of K_C and K_B kaolin samples show that $> 41\ \mu$, $> 30\ \mu$, $> 20\ \mu$, $> 10\ \mu$ and $< 3\ \mu$ particle size are 0.11, 1.33, 6.79, 27.99 and 36.94%, respectively. Kaolin samples are suitable for ceramic industry, paper-coating and paper-filling.

Colour measurement

Commercially valuable kaolin combines both, a desirable colour and a suitably fine particle size[12].

Pure kaolin occurs in nature as finely divided particulate dispersion of white colour. Kaolins are ubiquitously contaminated by small amounts, often 0.5–3% of impurities of ferruginous oxides, rutile, siderite, pyrite, mica and tourmaline[13]. Duvertepe kaolin raw materials contain impurities by small amounts (%), and if its concentration is above threshold, an unacceptable colouring masks the kaolin.

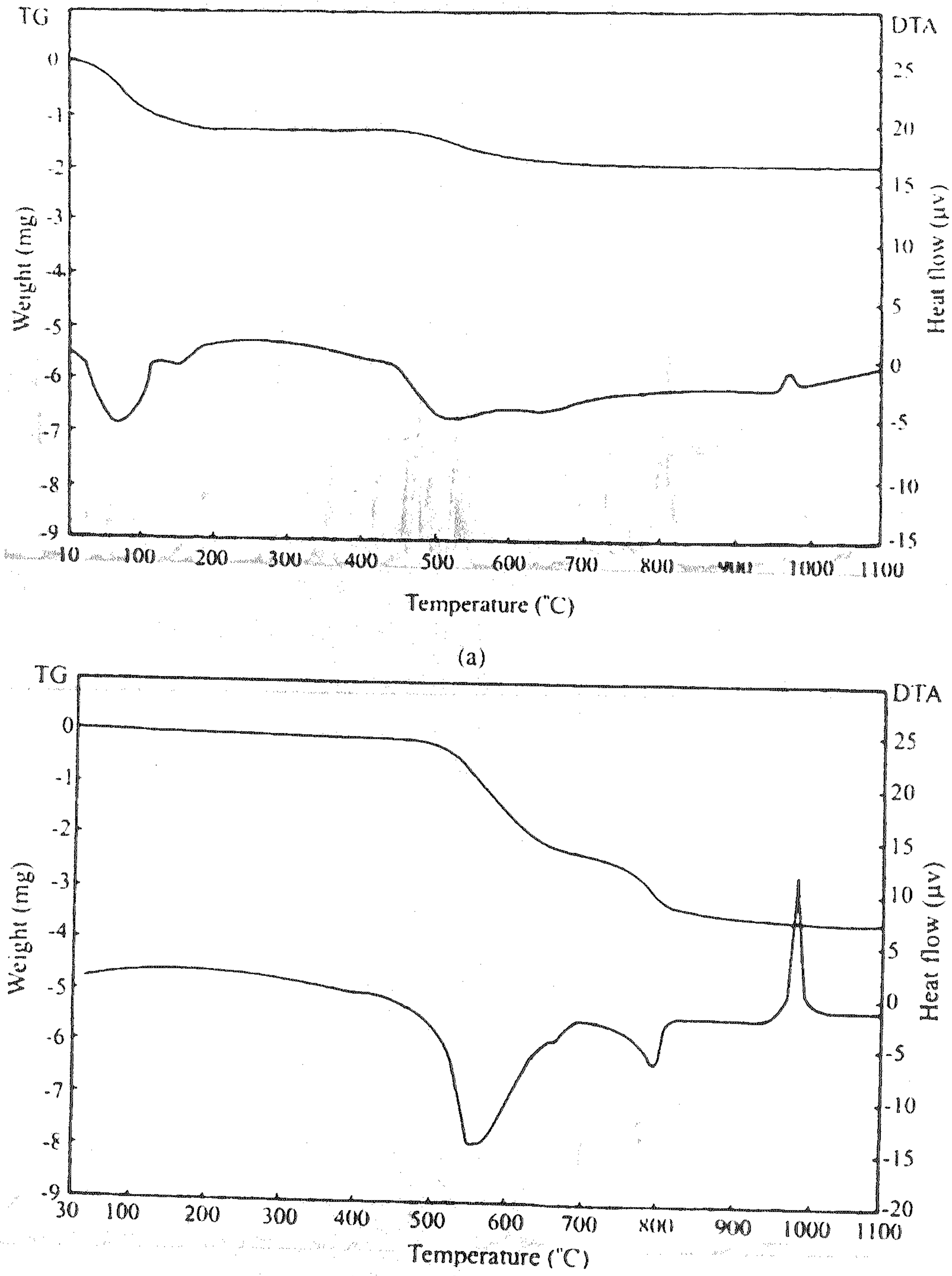


(a)

(b)

Fig. 1. Mineralogical analysis results: (a) K_C, (b) K_B. (K: Kaolin, Q: Quartz, M: Muscovite, A: Alunite, G: Goethite, I: Ilmenite, R: Ferric minerals)

The brightness of fired samples at different temperatures of K_C and K_B ranges from 92.80–94.82% and 88.95–95.25%, respectively (Tables 2 and 3). Brightness in excess of 80% would be required for kaolin to be used in paper-filling or paper-coating.



(a)

(b)

Fig. 2. TG-DTA thermogram of kaolin samples, (a) K_C (b) K_B

TABLE-2
COLOUR MEASUREMENT RESULTS OF K_C

Temperature (°C)	L	a	b
1000	92.80	+1.470	+2.70
1050	92.94	+1.310	+1.94
1100	93.89	+0.720	+1.45
1150	94.41	+0.330	+1.53
1200	94.90	+0.023	+1.40
1250	94.82	+0.008	+1.83

TABLE-3
COLOUR MEASUREMENT RESULTS OF K_B

Temperature (°C)	L	a	b
1150	88.95	+4.35	+4.88
1200	90.22	+3.14	+3.28
1250	91.96	+ 1.53	+2.75
1325	95.25	+0.24	+4.90

Plasticity

Plasticity changes the shape of a clay-water mass in non-elastic, non-reversible fashion[14]. As almost all of the clay materials are used in plastic state, the significant parameters include two of the Atterberg limits (the liquid limit, LL and the plastic limit, PL) and the plasticity index (PI). Plasticity index (PI) was calculated based on the arithmetic difference of the LL and PL of the kaolins. The LL and PL tests were carried out with a Casagrande apparatus using the method described by Casagrande[15]. LL value is calculated 47, 53; PL value 27, 29 and PI value 20, 24 for both kaolin samples (K_C, K_B), respectively.

Differential thermal and thermogravimetric analyses

The endothermic peaks at 30–110°C on curve C_C are attributed to loss of water and there is smectite at 110–225°C and characteristic peak of kaolin is seen at 500–700°C (Fig. 2a). The endothermic peaks at 500–600°C on the curve C_B are attributed to the characteristic peak of kaolin and that at 700–800°C shows alunite (Fig. 2b).

The DTA scans (K_C, K_B) showed that the analyzed samples had endothermic peaks between 500 and 600°C; 500 and 700°C, respectively, which is attributed to the dehydroxylation temperature of kaolinite. This situation can be explained by the transformation of kaolinite into metakaolinite, as expressed in eqn. (1).

The exothermic peak (K_C, K_B) at 900–1050°C corresponds to the temperature range for mullite from metakaolinite as eqn. (2). Both reactions were accompanied by mass loss for samples[16, 17].

$$\underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} \longrightarrow \underset{\text{Metakaolinite}}{Al_2Si_2O_7} + 2H_2O \qquad (1)$$

$$\underset{\text{Metakaolinite}}{Al_2Si_2O_7} \longrightarrow \underset{\text{Mullite}}{Al_6Si_2O_{13}} + 4SiO_2 \qquad (2)$$

Drying and firing shrinkage

Shrinkage on drying and firing at various temperatures is determined for the Duvertepe kaolin products. Shrinkage is related directly to the amounts of clay minerals and water in the plastic clay. Drying shrinkage is higher as compared to firing shrinkage. Firing shrinkage of K_C and K_B kaolin samples ranges from 0.85–1.80% and 2.10–5.55%, respectively. It slightly increases with the temperature of firing for each product (Figs. 3 and 4).

Firing behaviour

Firing induces no colour change in the pure samples of Duvertepe kaolin, but the samples with iron impurities turn light cream into buff.

Duvertepe kaolin possesses linear shrinkage of 1.80 and 5.55 and water absorption values of 19.55 and 19.06, respectively. The commercially used kaolin of Bavaria[5] exhibits linear shrinkage of 6–10 and water absorption of 12–21. The Duvertepe kaolin possesses some interesting properties for its applications in the ceramic sector, especially the quite low iron content and the moderate firing shrinkage.

In pure kaolin, the relationship between linear shrinkage (%) and water absorption (%} shows positive correlation as linear shrinkage increases with increasing percentage of water absorption. The Duvertepe kaolin is characterized by lower values of shrinkage and water absorption (Figs. 3 and 4). This behaviour is explained by the abundance of inert components such as mica, feldspar and ferric. Presence of these minerals leads to lower shrinkage with respect to hypothetical raw materials consisting entirely of kaolinite. Silica minerals show lower values of shrinkage and water absorption.

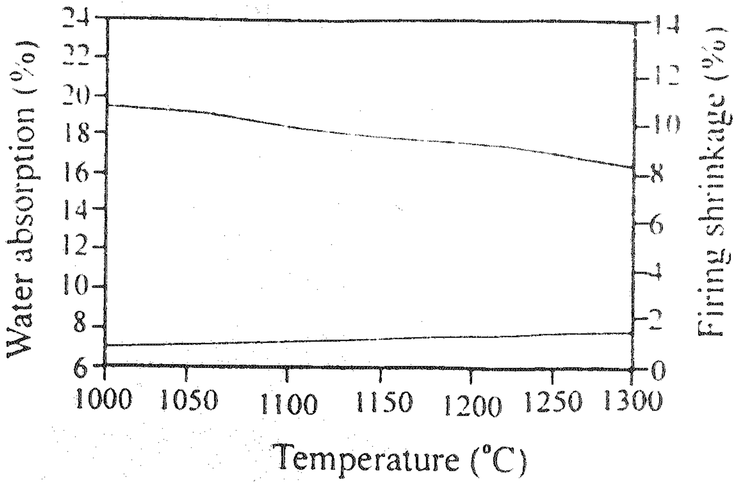


Fig. 3. Water absorption and firing shrinkage values of K_C at different temperatures

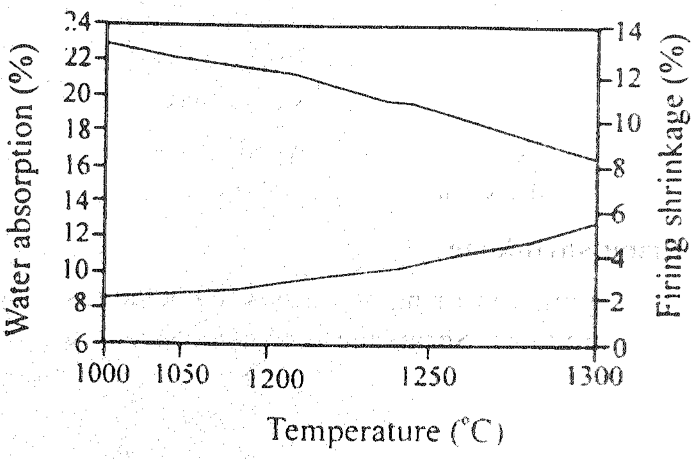


Fig. 4. Water absorption and firing shrinkage values of K_B at different temperatures

A general use of the Duvertepe kaolin could be to manufacture tiles and the richest in kaolinite are suitable for sanitary-ware manufacture.

Water absorption

The values of water absorption obtained for the Duvertepe kaolin are shown in Figs. 3 and 4. The water absorption values of briquettes fired at 1000°C are higher than those of briquettes fired at higher temperatures. At 1300°C, water absorption decreases to lower values and the porosity of the fired briquettes is low.

Conclusion

This evaluation of the Duvertepe kaolin deposits is based on the kaolin specific physical properties including the particle size, colour measurement viscosity, plastic limit, liquid limit, firing shrinkage, water absorption, volatile matter and chemical and mineralogical properties.

Kaolin finds diversified industrial uses, which are determined mainly by its physical properties[18], which, in turn, may depend on its chemical and mineral composition. Individual kaolin deposits possess characteristics specific for each[10, 19]. The key to ceramic use is low Fe_2O_3 content and a good fired brightness and casting rate. Although, SiO_2 and Al_2O_3 contents are slightly deviant.

The brightness for different uses of kaolin, after Bloodworth *et al.*[12], is specified as follows: paper coating, 81.5–90.5%; paper-filling, 76–82%; porcelain (at 1180°C) 95%; earthenware and tableware at (1180°C) 86%; sanitary-ware (at 1180°C) 82%. Specifications by Prasad *et al.*[11] range from 90–92% for paper coaling and 82–85% for paper filling. Highley[20] observed the required brightness values to be 83–91% for ceramic products (at 1180°C), 76–90% for paint filler, 70–92% for plastic filler, 70–92% for rubber filler, 76.5–84% for paper-filler, 85–88% for paper-coating clays, which require yellowness in the range of 4.2–4.7%.

Average brightness and whiteness of Duvertepe kaolin qualifies it as one of the best paper-coating materials which require minimal brightness of 80%[13]. The water absorption values of briquettes fired at 1000°C are higher than those of briquettes fired at higher temperatures. At 1280°C, water absorption decreases to lower values and the porosity of the fired briquettes is low. The firing behaviour of Swat kaolin after burning at 1280°C shows properties close to the specification of floor and wall tiles. Relatively pure Duvertepe kaolin samples exhibit low shrinkage and white firing colours required for the production of porcelain and wall and floor tiles.

Duvertepe kaolin is suitable for ceramic use in terms of the mineralogical, chemical composition and physical properties, inclusive of their firing shrinkage, colour and water absorption behaviour. It also could be used for glass production, fabrication of tiles, bricks, sanitary wares and structural materials.

REFERENCES

1. M.A. Siddiqui, Z. Ahmed and A.A. Saleemi, *Appl. Clay Sci.*, **29**, 55 (2005).
2. S. Chandrasekhar and S. Ramaswamy, *Appl Clay Sci.*, **21**, 133 (2002).
3. O. Castelein, B. Soulestin, J.P Bonnet and P. Blanchart, *Ceram. Int.*, **27**, 517 (2001).
4. G. Ekosse, *Appl. Clay Sci.* (Resource Note), **20**, 137 (2001).
5. P. Ligas, I. Uras, M. Dondi and M. Marisgli, *Appl. Clay Sci.*, **12**, 145 (1997).
6. DPT, 8th Five Year Development Plan Reports, DPT: 2611, ÖİK: 622 (2001).
7. BS 1377, The Method Test for Determination of Grain Size Distribution for Fine-grained Soils (1975).
8. H.H. Murray, *Acta Mineral.-Petrogr*, **24**, 67 (1980).
9. ———, *Appl. Clay Sci.*, **17**, 207 (2000).
10. ———, Clays in industry, in: E.A. Dominguez, G.R. Mas and F. Cravero (Eds.), A Clay Odyssey, Elsevier Science Publishers, Amsterdam, pp. 3–14 (2003).
11. M.S. Prasad, K.J. Reid and H.H Murray, *Appl. Clay Sci.*, **6**, 87 (1991).
12. A.J. Bloodworth, D.E. Highley and C.J. Mitchell, Kaolin. Tech. Rep.-Br. Geol. Surv., 76 (WG/93/1), (1993).
13. L. Toro, A.M. Maravini, B. Paponetti, B. Passariello, Processo per la rimozione del ferro da concentrati di caoline, quarzo ed altri materiali di interesse Indust.e, Italian Patent, 21707 A/90 (1990).
14. F. Moore, Rheology of Ceramic Systems, Maclaren & Sons, London, pp. 51–57 (1965).
15. A. Casagrande, *Trans. Am. Soc. Civ. Eng.*, **113**, 901 (1948).
16. P.R. Suitch, *J. Am. Ceram. Soc.*, **69**, 61 (1986).
17. M. Bellotto, A. Gualtieri, G. Artioli and S.M. Clark, *Phys. Chem. Minerals*, **22**, 207 (1995).Harvey,
18. W.M. Bundy, The diverse industrial applications of kaolin, in: H. Murray, W. Bundy and C. Harvey (Eds.), Kaolin: Genesis and Utilization, Vol. 1, Special Publication of the Clay Minerals Society, Colorado, USA, pp. 43–73 (1993).
19. H.H. Murray, W.D. Keller, Kaolins, kaolins and kaolins, in: H. Murray, W. Bundy and C. Harvey (Eds.), Kaolin: Genesis and Utilization, Vol. 1, Special Publication of the Clay Minerals Society, Colorado, USA, pp. 1–24 (1993).
20. D.H. Highley, China Clay Mineral Dossier, Vol. 26, British Geological Survey, UK (1984).

(*Received*: 14 July 2005; *Accepted*: 22 December 2005) AJC-4576