

Influence of mineral impurities on the properties of kaolin and its thermally treated products

Sathy Chandrasekhar*, S. Ramaswamy

Clays and Clay Minerals Section, Regional Research Laboratory (CSIR), Thiruvananthapuram (RRL, T) 695 019, India

Received 15 December 2000; received in revised form 29 May 2001; accepted 24 June 2001

Abstract

Kaolin or china clay is widely used in a number of industries due to its special properties like fine particle size, brightness and whiteness, chemical inertness, platy structure, etc. Raw kaolin is beneficiated to remove mineral impurities that affect these special properties. Kaolin—when thermally treated at specific temperatures—gives products of industrial significance called “calcined kaolin” with characteristic properties such as high brightness, hydrophobicity, abrasive nature and improved electrical properties. The present paper deals with the study of two Indian kaolins of different genesis. One of them is from Thiruvananthapuram district, Kerala, and the other from Kutch district, Gujarat. The latter one is of inferior quality due to the presence of ferruginous and titaniferous impurities and, therefore, subjected to high gradient magnetic separation. The beneficiated clay was also studied. The three samples were thermally treated under identical conditions at various temperatures. Calcined samples were analysed for their optical properties, pH, true and apparent densities and particle size distribution. The influence of iron and titanium containing impurities on the properties of the kaolins and their calcined products is discussed. The beneficiated Gujarat clay is found to be comparable with the Kerala clay. Calcination at 1100 °C gives products of similar optical properties. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Calcination; Kaolin; Brightness; Ferruginous impurity; High gradient magnetic separation

1. Introduction

Kaolin or china clay contains as the principal mineral kaolinite, which is a hydrated aluminium silicate ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). The Run-of-Mines (ROM) kaolin is beneficiated to different grades for making them suitable for various industries. The methods of beneficiation depend upon the quantity and nature of impurity minerals associated with the clay. The common techniques involve: (i) size classification

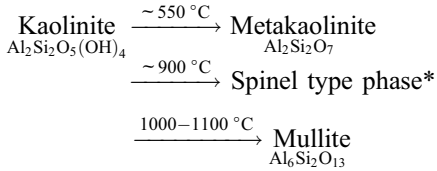
for removing coarse minerals and for attaining the specific particle size distribution, (ii) magnetic separation of the coloured minerals containing iron for improving the brightness, (iii) chemical bleaching for removing organic colouring impurities (oxidative) and iron minerals (reductive), and sometimes (iv) froth flotation to separate micaceous, graphitic and titaniferous minerals (Jepson, 1988). The beneficiation steps give a significant added value to the raw kaolin.

Thermal treatment or calcination of kaolin favourably changes its properties to obtain “calcined kaolin” with improved hydrophobicity, abrasive nature and good optical and electrical properties (Bundy,

* Corresponding author. Tel.: +91-471-515-329; fax: +91-471-491-712.

E-mail address: sathy@csrrlrrd.ren.nic.in (S. Chandrasekhar).

1993). Kaolinite undergoes the following reaction on thermal treatment:



where * indicates with separation of silica and/or other phases.

Calcination at low temperatures is essentially dehydroxylation of the kaolinite mineral resulting in the formation of an X-ray amorphous material called

metakaolinite. Further heating results in a spinel-type phase called primary mullite, which subsequently crystallises into mullite (Brindley and Nakahira, 1959; Newman, 1987). Calcination helps to develop higher brightness, hydrophobicity, improved light scatter, enhanced dielectric character and increased hardness.

The kaolins calcined at ~ 600 and $1100\text{ }^\circ\text{C}$ find applications in various industries such as paper, PVC coating on wire and cables, rubber, plastics, sealants, adhesives and also as polishing agents. Much higher opacity is imparted to paper by calcined kaolin (than kaolin) due to a high void content of fused aggregates,



Fig. 1. Location of the clay mines.

the open packing structure arising from irregular particle shape and also from the low colloid content. The improvement in dielectric properties finds its use in cable industry. Hydrophobicity is created during calcination and the surface chemistry becomes more compatible with organic systems. This property is made use of in rubber, plastics, etc. Increased hardness due to calcination permits use of fine particle calcined clay for polishing purposes such as in toothpaste, for automobiles and soft metals. The ceramic industry is also a good consumer of kaolin. The behaviour of clay during calcination is very important in hard and soft porcelains and also in bone china (Bundy, 1993).

A systematic study has been carried out on the influence of impurities especially the ferruginous/titaniferous minerals on the calcination of two Indian kaolins of industrial importance and having a different geological origin. The variation in properties was correlated with the impurity mineral content of the clays. Fig. 1 shows the locations of the different deposits.

1.1. Kaolin from Thiruvananthapuram district, Kerala State (KC)

This kaolin belongs to the upper tertiary sedimentary sequence (Warkalli formation) and is encountered in the coastal tract of Kerala. It is a weathering crust developed over the Khondalite–migmatitic complex. Sedimentological data suggest that kaolinite was transported and deposited in shallow waters with very high concentration of turbidites or highly turbid waters that suddenly lost transportation capacity (Soman, 1997). Coating grade kaolin is produced by M/s English Indian Clays (EICL) by beneficiating the clay from a secondary deposit at Thonnakkal, Thiruvananthapuram district. A representative sample is used for the present study.

1.2. Kaolin from Kutch district, Gujarat State (GC)

Kutch is well known in Indian geology because of typical exposures to Jurassic. The Jurassic formations are predominantly composed of alternating sequences of limestone, shale and sandstone of marine origin. The feldspathic sandstone of Bhuj series of Jurassic have undergone weathering resulting in the formation of kaolinitic clays, which are intermittently exposed in

various places of Kutch district. At some places, these clays contain impurities like Fe, Ti and Al minerals (Krishnan, 1997; GMCS Report, 1996). Nearly 10 tons of clay from a sedimentary deposit in this area has been collected, blended thoroughly and size classified using hydrocyclones. The product clay having ~ 90% particles below 2 μm has been selected for this investigation.

2. Experimental

The KC and GC samples were characterised for their physical, chemical and mineralogical properties. The latter contains more coloured mineral impurities of iron and titanium and was, therefore, beneficiated by Super Conducting High Gradient Magnetic Separation (SCHGMS) to get an improved product (GCB), which was also characterised. The three samples were calcined in a programmable muffle furnace at various temperatures (400–1200 °C) at an interval of 100°. A clay bed of 15 × 9 cm with a thickness of 0.5 cm, a heating rate of 6 °C per minute and a soaking time of 1 h were maintained for all samples during calcination. The following properties of the calcined samples were determined.

2.1. Particle size distribution analysis

Sieving and a Sedigraph 5100 (Micromeritics) were used for determining the particle size distribution in the clays and their calcined products.

2.2. pH

The pH of the clays and their calcined products were measured by the conventional method (IS 505, 1978).

2.3. Bulk density

The bulk density was measured using a graduated cylinder and 40 g of sample as described in the conventional method (IS 918, 1968).

2.4. True density

A Multivolume Helium Pycnometer (Micromeritics) was used for the true density measurements.

2.5. Optical properties (ISO)

The brightness, Hunter whiteness, yellowness and *Lab* colour values (unit ISO) were determined using a Colourtouch Model Spectrophotometer from Technidyne. Standard source *C* (whose spectral power distribution agrees well with that of the typical daylight) and an observer angle of 2° were chosen for these measurements.

2.6. Chemical analysis

Conventional wet chemical methods with instrumental techniques were followed for the chemical analysis of the clay samples (Bennett and Reed, 1971).

2.7. Mineralogy by XRD

An X-ray Diffractometer, Rigaku Model D_{max} , with Ni-filtered Cu K_{α} radiation, was used for determining the mineral contents of the clays and the phase formation during calcination.

3. Results and discussion

3.1. Properties of the clays

The characteristic properties of the three samples under study are given in Table 1. All the samples are highly kaolinitic and GC contains more impurity minerals than KC as indicated by the XRD analysis and chemical assay. The optical properties of GC are also inferior to those of KC. Our earlier studies on the GC clay have shown that part of the iron is in the TiO_2 structure and a good portion of it can only be removed by SCHGMS since the response of the clay towards reductive bleaching is poor (Chandrasekhar and Raghavan, 1999; Raghavan et al., 2000). The GC on SCHGMS treatment gives the product GCB with much improved optical properties due to the removal of iron and titania minerals. The quality comes up to a level of coating grade kaolin. The particle size distribution data indicates that GC and GCB samples have a higher percentage of the finer fraction (<2 μm). The true density values of the three clays are almost similar, but the bulk density of KC is lower.

Table 1
Characteristic properties of clay samples

Properties	KC	GC	GCB
Chemical assay (wt.%)			
SiO ₂	44.92	44.39	44.27
Al ₂ O ₃	37.45	37.98	37.91
Fe ₂ O ₃	0.45	0.43	0.28
TiO ₂	0.55	1.60	0.99
CaO	0.01	0.06	0.06
Na ₂ O	0.20	0.13	0.11
K ₂ O	0.04	0.02	0.015
LOI	14.68	14.31	14.40
Mineralogy (by XRD)	Kaolinite	Kaolinite, anatase	Kaolinite, anatase
Brightness (% ISO)	85.53	73.09	83.17
Particle size distribution (%)			
+45 μm	0.00	0.00	0.00
–45, +10 μm	0.00	0.00	0.00
–10, +5 μm	1.54	0.00	0.00
–5, +2 μm	13.25	10.00	8.85
–2 μm	85.21	90.00	91.15
True density (g/cc)	2.64	2.64	2.63
Bulk density (g/cc)	0.50	0.80	0.79
pH	6.02	7.14	7.44

The different processing conditions of the KC seems to be the reason for these differences. It is a commercial product of EICL and during processing the filter pressed cake is dried in a rotary drier. Air may be getting trapped between the clay particles making it porous. This results in a low bulk density (Searle and Grimshaw, 1960). On the contrary, the GC and GCB samples have been filtered and dried in a conventional air oven. The pH of KC is found to be lower than GC and GCB. Since H^+ ions are preferentially absorbed by clay particles, most natural clays contain H^+ , in part at least, as their exchangeable cations. Consequently, when such clays are suspended in water, dissociation occurs and the H^+ ion concentration in the suspension increases. The type of cations, which are present in natural clays, depends principally on the mode of formation and environment. Clay associated with lime strata will primarily have Ca^{2+} ions. Those derived from rocks containing alkali have predominantly Na^+ and K^+ ions. In clays which have been extremely leached or weathered, the exchangeable

Table 2
Particle size distribution of KC and its calcined products

Size fraction (μm)	Calcination temperature ($^{\circ}\text{C}$)									
	Clay	400	500	600	700	800	900	1000	1100	1200
+ 45	0.00	0.40	1.11	1.66	3.03	3.06	4.92	6.61	8.36	9.42
– 45, +20	0.00	0.00	1.90	1.51	2.61	2.06	1.83	2.88	2.82	1.74
– 20, +10	0.00	2.29	3.81	4.54	4.84	5.41	4.74	4.66	5.99	6.27
– 10, +5	1.54	7.24	6.47	7.56	6.71	6.71	8.04	7.55	8.11	8.02
– 5, +2	13.25	16.00	15.21	15.13	14.17	17.15	16.09	16.89	17.67	18.81
– 2	85.21	73.53	71.51	69.60	68.63	65.62	64.36	61.42	57.09	55.74

ions are mainly H^+ (Searle and Grimshaw, 1960). The GC and GCB samples belong to the first category and have higher Ca contents compared to KC and, hence, pH of the former is higher.

3.2. Properties of the calcined clays

3.2.1. Particle size distribution

The calcination of the clays at various temperatures affects most of the properties. The particle size distribution is significantly affected by the thermal treatment. Tables 2–4 give the size distribution of the uncalcined and calcined samples of KC, GC and GCB, respectively. The quantity of the coarse fraction increases with temperature in all the samples up to 800–900 $^{\circ}\text{C}$. At higher temperatures, particles are found to agglomerate more strongly producing a higher amount of coarse fractions in GC and GCB. The percentages of particles below 2 μm in the three samples have been plotted against the temperature of calcination as given in Fig. 2. During calcination, aggregate structures are formed by the partial fusion of particles. The important

factors affecting the fusion of clay are the size distribution of the particles and the presence of low temperature fusing materials (Ianicelli et al., 1999). The GC and GCB have a higher percentage of fines compared to KC and the ancillary mineral content is also higher. The higher particle agglomeration can, thus, be attributed to these factors. The temperature at which this agglomeration takes place was found to be 900–1100 $^{\circ}\text{C}$ for GC and 800–1100 $^{\circ}\text{C}$ for GCB.

3.2.2. XRD analysis

The XRD patterns of calcination products show that at 500 $^{\circ}\text{C}$, a small part of the kaolinite remains in the samples, which become totally amorphous at 1000 $^{\circ}\text{C}$. The amorphous structure remains almost unchanged with very small crystals of mullite in the samples calcined at 1100 $^{\circ}\text{C}$. Further heating to 1200 $^{\circ}\text{C}$ results in well defined peaks of mullite.

3.2.3. Density

The changes in bulk density and true density of the three clay samples on calcination are depicted in

Table 3
Particle size distribution of GC and its calcined products

Size fraction (μm)	Calcination temperature ($^{\circ}\text{C}$)									
	Clay	400	500	600	700	800	900	1000	1100	1200
+ 45	0.00	1.01	1.52	1.63	1.89	6.11	5.50	16.00	46.00	51.21
– 45, +20	0.00	0.00	0.76	0.79	1.13	1.45	1.46	4.52	4.15	3.37
– 20, +10	0.00	0.00	0.76	3.00	3.40	3.97	5.81	5.81	4.98	4.13
– 10, +5	0.00	0.00	3.03	3.40	3.40	3.97	5.81	6.46	3.74	3.38
– 5, +2	10.00	11.92	13.64	14.00	13.21	15.16	15.99	15.51	9.14	8.63
– 2	90.00	88.07	80.21	77.18	76.98	69.34	65.42	51.69	31.98	29.27

Table 4
Particle size distribution of GCB and its calcined products

Size fraction (μm)	Calcination temperature ($^{\circ}\text{C}$)									
	Clay	400	500	600	700	800	900	1000	1100	1200
+ 45	0.00	0.96	1.41	1.54	1.73	5.78	5.05	15.11	45.26	50.78
– 45, +20	0.00	0.00	0.00	0.79	1.13	1.45	0.00	1.31	2.46	3.94
– 20, +10	0.00	0.00	0.76	2.41	3.40	2.90	0.00	1.95	5.75	4.43
– 10, +5	0.00	0.00	1.52	3.38	3.40	2.90	2.01	4.24	4.11	4.92
– 5, +2	8.85	9.53	11.75	13.51	11.34	11.60	48.39	37.91	14.23	13.78
– 2	91.15	89.51	84.56	79.18	80.13	75.37	44.55	39.57	28.19	22.15

Figs. 3 and 4, respectively. On calcination, the bulk density of all samples gradually decreases with temperature. The bulk density of sample KC and its calcined products is much lower compared to the corresponding samples of GC and GCB. The percentage of coarser fractions is higher in GC and GCB. The difference in particle size distribution may also be contributing to the low bulk density of the calcined products of KC. The true density values show an increase with the calcination temperature. The sharp increase at ~ 900 and 1100 $^{\circ}\text{C}$ corresponds to the formation of a spinel type phase and mullite, respectively. The increase in density can also be due to particle aggregation (sintering). The density of single fragments of kaolin ranging in weight from about 5 to 25 g and their products of calcination at 1510 $^{\circ}\text{C}$ has been reported by Baumann and Keller (1975). The silica released during mullitisation combines with alkali, alkaline earth, iron and

other metal cations to form a siliceous glass in which the mullite crystals are embedded. The density of mullite is 3.2 and that of silicate glass is ~ 2.4 (or higher as the iron content increases). The density values of GC and its calcined products are found to be slightly higher than the corresponding samples of KC and GCB, which can clearly be attributed to the higher impurity (Fe and Ti) content in the former.

3.2.4. pH

On calcination, the pH values firstly decrease with temperature up to 600 $^{\circ}\text{C}$ and then increase in all the three samples as shown in Fig. 5. The decrease in pH in the metakaolinitic stage is possibly due to the kaolinite rehydroxylation utilising the OH groups displaced (Velho and Gomes, 1994). The pH values are different for the clay samples but the calcination products at 700 and ≥ 1100 $^{\circ}\text{C}$ are found to be al-

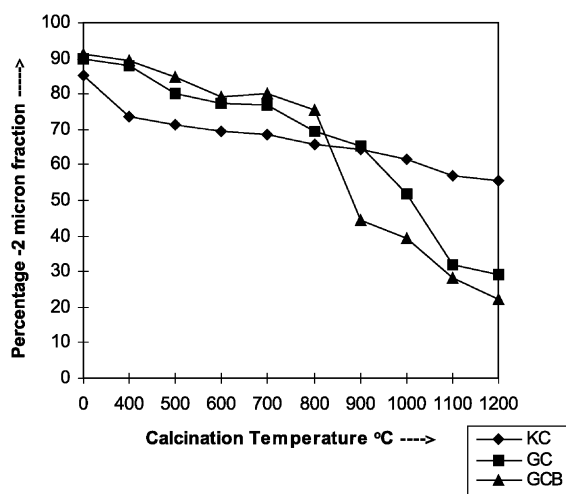


Fig. 2. Variation of $-2\text{-}\mu\text{m}$ fraction with calcination temperature.

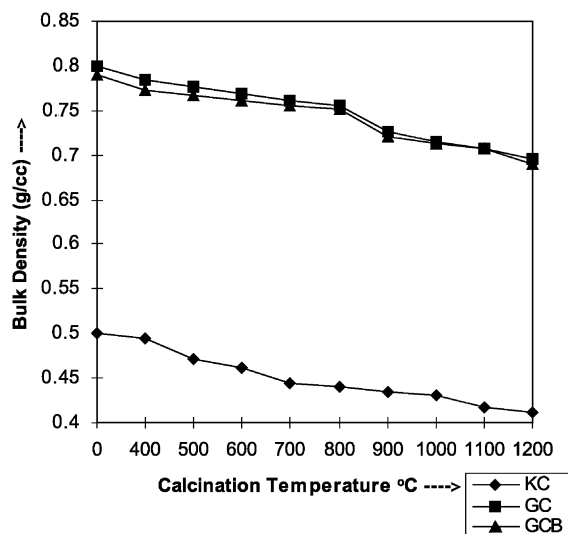


Fig. 3. Change in bulk density with calcination temperature.

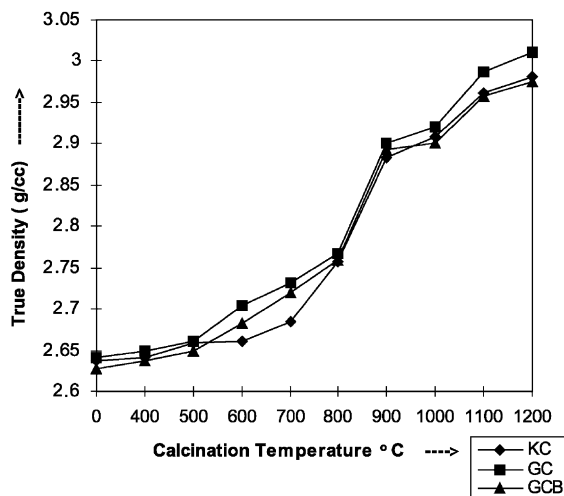


Fig. 4. Change in true density with calcination temperature.

most the same. The former temperature corresponds to the formation of metakaolin and the latter to that of mullite.

3.2.5. Optical properties

The important optical properties include brightness, whiteness, yellowness and the ‘colour values’ L , a and b and are expressed in ISO units. Brightness is the percentage reflectance of light at a wavelength of 457 nm and the difference in reflectance values at 457 and 570 nm gives the yellowness. Hunter whiteness and yellowness indices have the advantage of

being single number quantities that are based on the entire visible spectrum. The whiteness formula relates better to people’s visual assessment than brightness whereas yellowness indices do not normally correlate well with visual judgement of yellowness. The *Lab* system based on the idea of colour opposites has been developed to give a better representation. The term L is a measure of lightness/darkness and varies from 100 for perfect white to 0 for absolute black. The red/green colour is indicated by a (the more positive the value of a , the greater the reddishness and the more negative the more greenishness). The yellow/blue shade is represented by b (the positive value gives yellowness and the negative corresponds to blueishness).

The optical properties of KC and its calcined products are found to be superior to those of GC. The beneficiation by SCHGMS enhances the quality of the latter clay and subsequent thermal treatment (of the GCB) gives rise to products that are comparable to those of KC. This finding is of great industrial significance. The brightness values of the clays and their calcined products are plotted against the temperature of calcination as represented by the Fig. 6. During calcination, the brightness firstly decreases with the temperature up to 500/600 °C and then increases. The value reaches a maximum at 1100 °C for all the clays and then slightly decreases at 1200 °C. Sudden rise in brightness with the temperature from 1000 to 1100 °C in all the samples is quite conspicuous. The colour values such as yellowness and the *Lab* values are inversely related to the brightness and show a similar

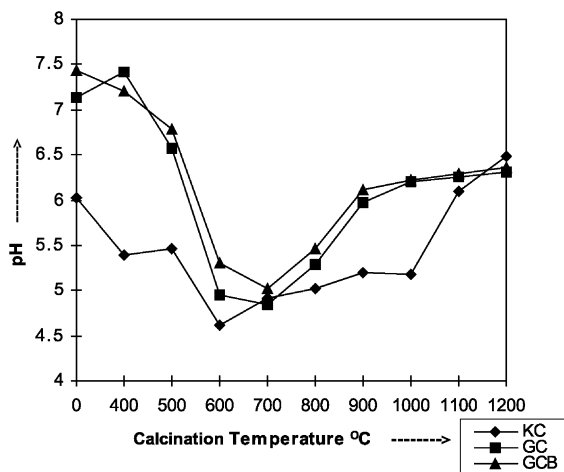


Fig. 5. Change in pH with calcination temperature.

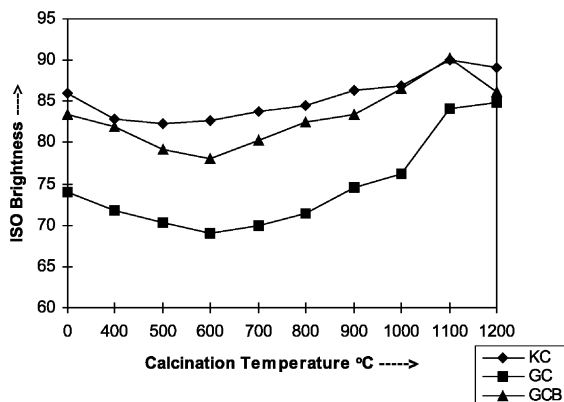


Fig. 6. Change in brightness with calcination temperature.

trend. The Hunter whiteness and yellowness of the samples are depicted in Figs. 7 and 8, respectively and Table 5 gives the *Lab* values. The KC and GC samples and their calcined products have positive values for *a* and *b* indicating the reddishness and yellowness and the GC samples have much higher values. But the SCHGMS treatment has brought down both values and *a* goes to negative in most of the calcined products of GCB. This significant decrease in reddishness can be attributed to the removal of some free iron oxide impurities along with the titaniferrous minerals. The reduction in iron content from 0.43 to 0.29 (Fe₂O₃) by SCHGMS treatment of the GC sample supplements this observation.

In clays, the light absorption occurs when colouring contaminants such as transition metal ions and organic and other carbonaceous impurities are present. On the other hand, light scattering enhances when the surface area increases, i.e. when the particle size is reduced. In the sample GC, the average size of the particles is smaller and the fine fraction is more comparable to that of the KC. But the effect due to this is masked by the higher light absorption due to the presence of more colouring impurities. It is interesting to note that in spite of having almost the same ‘analytical iron’ content, the clays GC and KC differ very much in their optical properties. However, on beneficiation, the iron and titanium contents considerably decrease and the sample GCB becomes

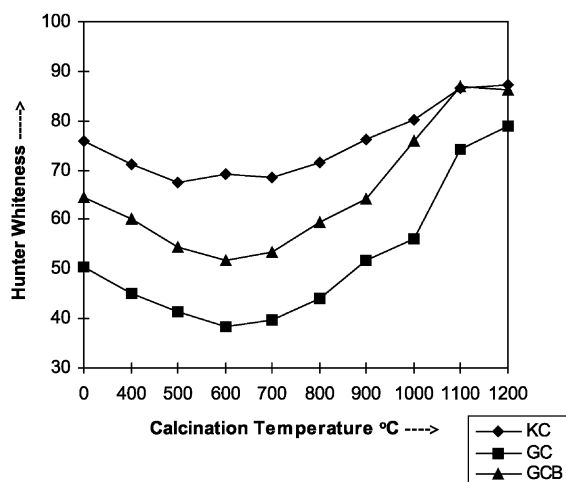


Fig. 7. Change in Hunter whiteness with calcination temperature.

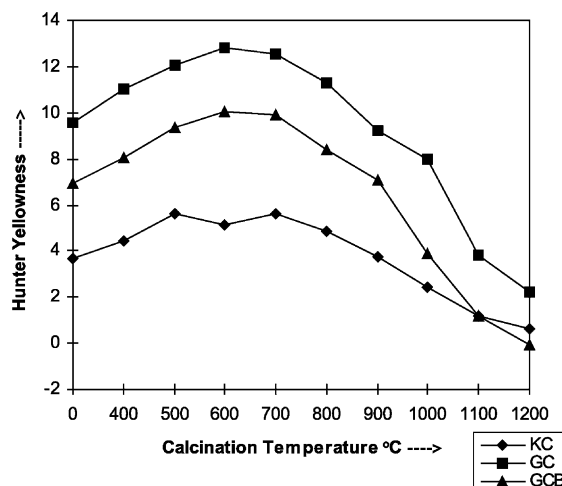
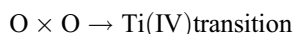


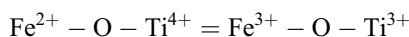
Fig. 8. Change in Hunter yellowness with calcination temperature.

comparable to KC in the optical properties but with less iron and more titanium. This observation clearly indicates that it is not the ‘quantity’ of iron but the ‘nature or species’ which influences the brightness of clay.

Pure TiO₂ does not absorb light in the visible region but strongly absorbs in the UV region due to the metal oxygen charge transfer process in the reaction:



When iron is present in the structure of TiO₂, a Fe(II) → Ti(IV) transition is possible. It has been reported that when Fe and Ti are present together in a glass, a charge transfer or electron hopping process takes place between Fe and Ti ions via an intermediate oxygen ion (Hogg and Noble, 1979).



This charge transfer process has an absorption centred at 350 nm in the near-UV region tailing into the visible at the blue end of the spectrum. Intensities of charge transfer bands are reported to be 100–1000 times stronger (in terms of extinction coefficient) than other transitions like d–d type. Thus, the amount of iron may be small but it has a major effect on the shade of kaolin, which is called ‘Titania effect’ (Weaver, 1976). KC has a lower TiO₂ content and almost same

Table 5
Optical properties—*L*, *a*, *b* values of KC, GC and GCB and their calcined products

Temperature of calcination (°C)	KC			GC			GCB		
	<i>L</i>	<i>a</i>	<i>b</i>	<i>L</i>	<i>a</i>	<i>b</i>	<i>L</i>	<i>a</i>	<i>b</i>
–	94.44	0.20	2.48	90.33	0.61	6.06	94.68	–0.29	4.85
400	90.30	0.48	2.92	89.62	1.24	6.90	94.21	–0.02	5.32
500	93.29	0.46	3.65	89.20	1.61	7.51	93.23	0.06	6.09
600	93.22	0.48	3.33	88.73	1.94	7.96	92.89	–0.08	6.53
700	94.11	0.67	3.70	89.19	2.48	7.83	94.15	0.27	6.52
800	94.20	0.92	3.21	89.60	2.27	7.09	94.71	0.36	5.78
900	94.67	0.91	2.46	90.46	2.02	5.84	94.62	0.02	4.69
1000	94.32	0.76	1.60	90.89	1.79	5.09	94.73	–0.28	2.56
1100	95.45	0.40	1.20	93.48	1.18	2.49	95.50	–0.38	0.78
1200	94.65	–0.20	0.42	93.08	–0.09	1.46	92.74	–0.38	–0.03

Fe₂O₃ percentage and a much higher brightness than GC. Most of the iron in KC may be possibly in the kaolinite structure and hence may not be affecting the brightness. The SCHGMS treatment of GC brings down both the iron and titanium percentage. When the samples KC and GCB are compared, the latter contains less iron, more Ti and has a slightly less brightness. This confirms that it is the iron-containing titanium (titaniferous) mineral which affects the optical properties of the GC sample.

On calcination, the kaolinite structure breaks down and the iron-containing minerals are converted to free oxides that impart colour to the product. Sometimes the organic matter released from the kaolinite particles also contributes to this. Thus, the optical properties degrade during initial heating. Then, as the temperature is increased, the position of iron changes during dehydroxylation and with its incorporation into the mullite structure, the organic matter, if any, burns off and the optical properties improve significantly (Stoch, 1987). The minimum brightness (maximum colour) is at 600 °C for GC and GCB samples and at 500 °C for KC. The sharp improvement in the optical properties for all the samples in the 1000–1100 °C range agrees well with the crystallisation of mullite as indicated by the XRD studies. During this process, the iron and titanium go into the mullite structure. The increase in brightness percentage is much more in GC and corresponds to the higher quantity of Fe and Ti going into the mullite structure. At 1200 °C, the trend of a decrease in *a* and *b* values is continued, but also the *L* value shows a decrease. This contributes to the lowering in brightness. Incidentally, this decrease is

found to be less for KC compared to the GC and GCB samples.

4. Conclusions

(i) The china clays KC and GC are highly kaolinitic but differ in their particle size distribution and ancillary mineral content. The GCB produced by the SCHGMS treatment of GC is found to have properties closer to those of KC.

(ii) On calcination, the GC and GCB samples are found to undergo more aggregation compared to KC, which can be attributed to the finer particle size and presence of more ancillary minerals in the former two samples and the different processing conditions of the latter.

(iii) The changes in pH and density of the clays on calcination show almost a similar trend in all the samples.

(iv) The optical properties of GC were found to be inferior to KC in spite of having the same iron content. The percent titania is much higher in the former and it is the 'iron-containing titania' in GC, which brings down the optical properties. However, SCHGMS reduces the iron percentage to a lower level than that in KC, but the reduction in titania percent is not that high. These titania particles with iron in their structure influence the white shade of clay and makes it inferior to KC.

(v) Calcination increases the brightness and whiteness and decreases the colour values giving an overall improvement in optical properties. Calcina-

tion at 1100 °C gives maximum brightness and KC and GCB give products with almost similar optical properties.

Acknowledgements

The authors are thankful to Mr. P. Raghavan, scientist at the RRL, T for providing the beneficiated GC samples for this investigation. Thanks are also due to the Director of the RRL, T for his permission to publish these research results.

References

- Baumann, D., Keller, W.D., 1975. Bulk densities of selected dry natural and fired kaolin clays. *Clays Clay Miner.* 23, 424–427.
- Bennett, H., Reed, R.A., 1971. *Chemical Methods of Silicate Analysis*. Academic Press, London.
- Brindley, G., Nakahira, M., 1959. The kaolinite–mullite reaction series—I. A survey of outstanding problems. *J. Am. Ceram. Soc.* 42, 311–324.
- Bundy, W.M., 1993. The diverse industrial applications of kaolin. In: Murray, H.H., Bundy, W.M., Harvey, C.C. (Eds.), *Kaolin Genesis and Utilisation*. Special Publication of the Clay Mineral Society, Colorado, USA, vol. 1, pp. 43–73.
- Chandrasekhar, S., Raghavan, P., 1999. Characterisation of ancillary minerals in Kutch kaolin during size classification. In: Sastry, S.R.S., Mohanty, S., Mohapatra, B.K. (Eds.), *Proc. of the Int. Symp. on Beneficiation, Agglomeration and Environment (ISBAN-99)*. Allied Publishers, New Delhi, India, pp. 24–31.
- Gujarat Mineral and Consultancy Services, 1996. Unpublished report.
- Hogg, C.S., Noble, F.R., 1979. A Kubelka–Munk analysis of the influence of iron and titanium oxides on the optical properties of hard porcelain. *Science of Ceramics*, vol. 10. Berchtesgaden, Germany, pp. 703–710.
- Ianicelli, J., Williamson, J.T., Pechin, J., 1999. Conversion of black underclays from Shanxi Province PRC to high brightness calcined clay. *Proc. Annual Session of the Clay Mineral Society, Purdue University (US)*, June 26–July 1.
- IS 505, 1978. Specifications for light kaolin.
- IS 918, 1968. Specifications for precipitated calcium carbonate for cosmetic industry.
- Jepson, W.B., 1988. Structural iron in kaolinites and in associated ancillary minerals. In: Stucki, J.M. (Ed.), *Iron in Soils and Clay Minerals*. Reidel, Dordrecht, The Netherlands, pp. 467–536.
- Krishnan, M.S., 1997. *Geology of India and Burma*, 6th edn., CBS Publishers and Distributors (Delhi), New Delhi, India.
- Newman, A.C.D., 1987. *Chemistry of Clays and Clay Minerals*. Mineralogical Society Monograph, vol. 6. Wiley, New York, USA.
- Raghavan, P., Chandrasekhar, S., Ramaswamy, S., 2000. Processing of china clay by superconducting high gradient magnetic separation. In: Bhattacharya, P., Singh, R., Goswamy, N.G. (Eds.), *Proc. Int. Symp. on Processing of Fines*. NML, Jamshedpur, pp. 108–113, Published by Director.
- Searle, A.B., Grimshaw, R.W., 1960. *Chemistry and Physics of Clays*. Western Printing Services, Bristol.
- Soman, K., 1997. *Geology of Kerala*. Geological Society, India.
- Stoch, L., 1987. Iron in kaolins—mineralogical, crystallo-chemical and technological aspects. *Interceram* 6, 21–25.
- Velho, J.A.L., Gomes, C.S.F., 1994. Influence of calcination on physical and technological properties of kaolins for paper filler applications. *Geol. Carpathica-Clays* 45 (1), 21–26.
- Weaver, C.E., 1976. The nature of TiO₂ in kaolinite. *Clays Clay Miner.* 24, 215–218.