CORRELATION BETWEEN CHROMOPHORE IMPURITY CONTENT AND FIRED COLOUR DATA OF KAOLIN CLAY

PARVESH AGRAWAL

*Central Glass & Ceramic Research Institute, 168-169, Naroda Industrial Estate, Naroda,
 Ahmedabad, Gujarat 382330, India.
 parvesh@cgcri.res.in*

S. N. MISRA

*Central Glass & Ceramic Research Institute, 168-169, Naroda Industrial Estate, Naroda,
 Ahmedabad, Gujarat 382330, India.
 snmisra@cgcri.res.in*

T. SHARMA

*Department of Fuel and Mineral Engineering, ISM University Dhanbad
 Dhanbad, Jharkhand, India
 hodfmeism@yahoo.co.in*

Different kaolin clay specimen exhibit varying colours after firing depending upon the relative presence of different mineral impurities, physical state of mineral constituents etc. Spectrophotometers used for determining colour values generate many sets of colour data. Interpretation of such colour values is a subjective matter. Increase in darkness, yellowness etc as a consequence of increase in chromophore impurity content in kaolin clay have been shown. However, the inverse of above ie; gradual change in colour values along with gradual change in chromophore impurity content over a realistic range has not been studied. Whether the colour data of kaolin clay after firing can be taken up as a function of impurity content needs to be investigated. Thus, to identify the correlation between kaolin clay impurity content and its fired colour data the present investigation examined the hypotheses i) The colour development after firing of kaolin clay is an indicator of chromophore impurity content present therein and ii) All the colour variables (L, a, b, ISO2470, redness) constituting a colour data set of pressed kaolin clay specimen after firing will vary in similar manner such that to represent variation in impurity content. The study indicated that the colour values obtained by spectrophotometry of clay specimens after firing represent the chromophore impurity present therein in a less reliable manner. To relatively estimate the quantity of chromophore impurity present in a clay sample from its fired colour, the sample should be mixed with 50% by weight of potash feldspar, pressed in to tablet suitable for colour measurement and fired at or above 1220°C to vitrify. After that the 'L', 'a' and 'ISO2470' values obtained truly represent the chromophore present therein.

Keywords: Kaolin; Spectrophotometry; Fired colour.

Introduction

The basic structure and composition of ceramic have an influence on the way light interacts with them. Clay based ceramic bodies e.g.; porcelain contains small crystals

embedded in glassy matrix. The relative amount of crystals and glass depends upon the process of preparation including composition of the mix. The relative amount of all the present phases crystal glass and pores and their morphology coupled with physical properties of constituent phases contribute to overall colour of ceramic.¹

Different kaolin clay specimens exhibit varying fired colours depending upon the relative presence of different mineral impurities, physical state of mineral constituents, firing temperature etc in them. Spectrophotometers used for determining colour values generate many sets of colour data. Interpretation of such colour values is a subjective matter. Researchers have shown increase in darkness, yellowness etc as a consequence of increase in chromophore impurity content in kaolin clay.²⁻⁴ However, the inverse of above ie; gradual change in colour values along with gradual change in chromophore impurity content over a realistic range has not been studied. Whether the colour data of kaolin clay after firing can be taken up as a function of impurity content needs to be investigated. To identify the correlation between kaolin clay impurity content and its fired colour data, and fix up the appropriate experimental conditions for determination of fired colour of kaolin clay, an investigation has been carried out to examine the hypotheses; 1) The colour development after firing of kaolin clay is an indicator of chromophore impurity content present therein, 2) All the colour variables (L, a, b, ISO2470, redness) constituting a colour data set of pressed kaolin clay specimen after firing will vary in similar manner such that to represent variation in impurity content.

Experimental

Materials and Methods

About 500 grams of low grade china clay SR, which is high in chromophore minerals, was pulverised and powdered material was blunged in water keeping 10% solid concentration and 0.5% sodium hexameta phosphate on weight basis of clay was added as dispersant. The clay was dispersed with the help of an electrical stirrer (200rpm). The thoroughly dispersed slip was passed through 53 μ (300 mesh) sieve and the -53 μ fraction was obtained. The material retained on the sieve discarded. The slip was dewatered and dried. The -53 μ fraction was further subjected to a high shear treatment to separate fine grained chromophore impurities and kaolin platelets in a laboratory model high shear mixer rotating at 2000 rpm. The high shear treatment was carried out at 65% solid concentration, 0.4% addition of sodium silicate dispersant and for 4 minutes duration. Then the treated slurry was diluted with tap water to attain solid concentration of 10%. The slurry was allowed to stand undisturbed for 10 minutes and coarse, heavy impurities were allowed to settle. Then, the clay suspension on the top was decanted and settled impurities in the bottom were collected separately. This process of separating impurity fraction repeated until there remained no traces of impurities. Both the fractions dewatered, dried and reserved for further experiments. The chromophore impurity fraction was incorporated in purified kaolin clay fraction in gradually increasing amount as given in Table 1 and total nine numbers of batches were obtained.

Table 1: Controlled addition of chromophore impurity fraction in purified kaolin clay fraction

Batch No. $\Rightarrow$	I	A	B	C	D	E	F	G	J
Purified clay fraction, wt. %	100	90	80	70	60	50	40	30	0
Impurity fraction, wt. %	0	10	20	30	40	50	60	70	100

All the nine batches were divided in to two parts and one part of each mix was further mixed with equal amount of potash feldspar, (1:1 ratio). All the 'clay only' batches and 'clay and feldspar' batches were mixed thoroughly and homogenised by dispersing in sufficient water, drying up to 7% moisture content and making dust for pressing. The dust was pressed uniaxially to form a tablet of 10 mm dia and 5 mm thickness in a manually operated laboratory model hydraulic press at 5 kg cm⁻² sp pressure. The pressed and dried tablets were fired at 1180°C, 1200°C, 1220°C, 1240°C and 1260°C in an electric kiln heated at 10°C per minute rate with dwelling of 15 minutes at peak firing temperature.

The SR purified clay and impurity fractions were characterised for complete chemical analysis, X ray powder diffraction (XRD), approximate mineralogical constituents were calculated by rational analysis, Particle size distribution, FTIR analysis, Thermo gravimetric and differential thermal analysis as per standard procedures. The optical properties ie; L,a,b in ISO units, ISO2470 whiteness index and redness were measured by spectrophotometer.

Result and Discussion

The chemical analyses of SR (-53 μ), high shear treated purified clay SR (HSPC) and its impurity fractions (HS-IMP) and feldspar are presented in Table-2. The XRD, DTA and FTIR patterns of SR (-53 μ), HSPC and HSIMP are shown in Fig.1-3 respectively. The

Table 2: Chemical Analysis of Different Clay Fractions and Feldspar

Clay Fractions $\Rightarrow$	SR (-53 μ)	HSPC	HS- IMP	Feldspar
SiO ₂	47.40	45.33	52.06	66.54
Al ₂ O ₃	35.60	36.77	30.97	18.68
Fe ₂ O ₃	1.17	0.72	0.95	0.36
TiO ₂	2.71	2.07	2.96	0.05
CaO	0.11	0.6	0.6	1.12
MgO	0.12	0.08	0	0.08
K ₂ O	0.50	0.19	0.43	10.03
Na ₂ O	0.14	0.19	0.17	2.85
LOI	11.99	14.05	11.86	0.29

Fig. 1: XRD curves of SR (-53μ), HSPC and HSIMP clay fractions.

Fig. 2: DTA curves of SR (-53μ), HSPC and HSIMP clay fractions.

Fig. 3: FTIR curves of SR (-53μ), HSPC and HSIMP clay fractions.

XRD pattern of SR (-53 μ) clay fraction shows sharp peaks at $d = 7.13, 3.57, 2.56, 2.28, 1.67$ and $1.54 \text{ \AA}$ due to kaolinite and $d = 3.34, 4.25 \text{ \AA}$ due to quartz. Strong peaks at $d = 3.57, 2.38$ and $1.89 \text{ \AA}$ are due to anatase. Three weak bands at $d = 4.17, 3.84$ and $1.78 \text{ \AA}$ are due to Haematite / siderite as the major iron bearing impurity.

The DTA curves of SR (-53 μ), HSPC and HSIMP exhibited characteristic endothermic and exothermic peaks of kaolinite at around 540°C and 995°C respectively. Comparing with theoretical value of dehydroxylation weight loss of kaolinite; 13.9% with that of SR (-53 μ), it appears to be moderately contaminated with non clay matter. Area under the dehydroxylation curve at around 540°C indicates the relative quantity of kaolinite. The same was in the order of $\text{HSPC} > \text{SR} (-53\mu) > \text{HSIMP}$. The primary mullite peak shifting to the lower temperature by 1°C in HSPC is attributed to higher reactivity through finer particle size distribution.

Based on mineral identified by XRD, TG/DTA and chemical analysis, the quantitative estimation of mineral constituents in the four clay fractions was carried out by norms method and presented in Table 3. The kaolinite content has gradually increased from 88.41% in SR (-53 μ) to 91.79% in HSPC. The free silica content reduced from 3.63% in SR (-53 μ) to 0.77% in HSPC. It is evident that through high shear treatment the clay is efficiently separated from non clay matter and chromophore impurities. The particle size analysis of the three clay fractions (Fig.4) revealed that the concentration of particles in the finer size ranges of 15μ and 10μ has increased in HSPC from SR (-53 μ). Based on 0.77% free silica and 91.79% kaolinite content (rational analysis), the HSPC is considered pure clay. Its particle size distribution showed all the particles to be below 10μ in size. Hence it is inferred that impurity content of free silica, haematite and anatase etc are more concentrated in the size range of 10μ to 36μ .

The chemical analysis and rational analysis of all the experimental batches was calculated and the five colour variables were plotted against Kaolinite content, Haematite content and rutile content for both the 'clay only' and 'clay and feldspar' specimens. The variation of colour variables with respect to variation in kaolinite content and chromophore impurity content on a linear scale was observed. For clay only specimens, plot of 'L' versus kaolinite content showed R^2 (confidence level) values greater than 90%

Table 3: Rational analysis of different clay fractions and feldspar

Clay Fractions	SR (-53 μ)	HSPC	HS- IMP	Feldspar
Kaolinite	88.41	91.79	76.53	7.94
Quartz	3.63	0.77	13.80	7.89
Feldspar	4.15	2.73	3.98	81.70
Calcite	0.20	1.07	1.07	1.96
Magnesite	0.25	0.17	0.00	0.17
Rutile	2.72	2.07	2.96	0.05
Haematite	1.17	0.72	0.95	0.35
Carbonaceous	0.54	0.68	0.71	0.00

Fig. 4: Particle Size Distribution of Different Clay Fractions

at 1260°C (Fig. 5). All other plots either showed no specific trend or lesser than 90% confidence level. It has been reported in case of brightness of calcined kaolin that the calcinations temperature influences the solubility of iron and the brightness and reactivity of metakaolin.⁵ The brightness of kaolin changes during firing. From about 350°C to 800°C the brightness is reduced generally however in case of kaolin without free Fe_2O_3 , it remains reduced up to 500°C only. Above these temperatures, the brightness increases with the firing temperature under oxidising conditions because of iron going into structure of the phase.⁶

Fig. 5: Plot of 'L' values v/s Kaolin content for clay only specimen

Plot of 'a' with respect to kaolin, haematite and rutile presented in Fig. 6, 7 and 8 showed varying trends with confidence level fluctuating between 87% to 98%, however above 1240°C, the confidence level remained greater than 90%.

Fig. 6: Plot of 'a' values v/s Kaolin content for clay only specimen

Fig. 7: Plot of 'a' values v/s Haematite content for clay only specimen

Fig. 8: Plot of 'a' values v/s Rutile content for clay only specimen

Plot of 'b' values with different fix parameters did not yield any trend (Fig. 9). Plot of 'ISO2470' with respect to 'kaolin content' showed maximum confidence level of 87% only at 1260°C (Fig. 10).

Fig. 9: Plot of 'b' values v/s Rutile content for clay only specimen

Fig. 10: Plot of 'ISO2470' values v/s Kaolin content for clay only specimen

For 'clay and feldspar' samples, plot of 'L' versus Kaolin content (Fig. 11) showed the 'L' values to vary with kaolinite content linearly with a confidence level of greater than 95% on all the firing temperatures $\geq 1220^\circ\text{C}$. Plot of 'L' vs Haematite (Fig. 12) and 'L' vs Rutile (Fig. 13) showed 92.4% and 94.3% confidence level at 1220 °C. Plot of 'ISO2470' values with respect to kaolin content (Fig. 14) showed confidence level of 91.7%, 92.9% and 91.3% at firing temperatures of 1220°C, 1240°C and 1260°C respectively. Plot of 'b' values (Fig. 15) and 'redness' values (Fig. 16) against kaolin, haematite or rutile etc. did not show any adequate trends.

Fig. 11: Plot of 'L' values v/s Kaolin content for 'Clay and Feldspar' specimen

Fig. 12: Plot of 'L' values v/s Haematite content for 'Clay and Feldspar' specimen.

Fig. 13: Plot of 'L' values v/s Rutile content for 'Clay and Feldspar' specimen.

Fig. 14: Plot of 'ISO2470' values v/s Kaolin content for 'clay and felspar' specimen.

Fig. 15: Plot of 'b' values v/s Haematite content for 'clay and felspar' specimen.

Fig. 16: Plot of 'Redness' values v/s Haematite content for 'clay and felspar' specimen.

Conclusion

1. Based on above discussion it is inferred that the variation in colour values of kaolin clay specimens after firing is not linear exactly.
2. The colour values obtained by spectrophotometer of clay only specimens after firing represent the chromophore impurity present therein in a less reliable manner. These values may be misleading if different types of clays are compared.
3. The colour values of L, a and ISO2470 of clay specimens obtained in vitreous condition truly represent the chromophore impurity present therein.
4. To relatively estimate the quantity of chromophore impurity present in a clay sample with its fired colour, the sample should be mixed with 50% by weight of potash feldspar, pressed in to tablet suitable for colour measurement and fired at or above 1220°C so as to vitrify. After that the 'L', 'a' and 'ISO2470' values obtained truly represent the chromophore present therein.

Acknowledgments

The authors are thankful to the Director, CGCRI, Kolkata for his constant encouragement and permission to publish the paper. Authors are also thankful to chemical laboratory, Material Characterization Lab, and XRD division (Kolkata) for their co-operation for various testing activities in connection to this study.

References

1. Stevenson, B. The colour measurement of ceramic samples using a commercial colour measuring device and a laboratory spectrophotometer,. PhD desertation, University of Eddinburgh., Eddinburgh, 2009.
2. Sathy Chandrashekhar, S. R., Influence of mineral impurities on the properties of Kaolin and its thermally treated products. *Applied clay science* **2002**, 21, 133-142.
3. P Raghavan, S. C., V.Vogt, E.Gock Separation of titaniferous impurities from kaolin by high shear pretreatment and froth flotation. *Applied clay science* **2004**, 25, 111-120.
4. J. A. Gonzalez, M. D. C. R., Bleaching of kaolins and clays by chlorination of iron and titanium. *Applied clay science* **2006**, 33, 219-229.
5. S. Chandrashekhar, Influence of metakaolinisation temperature on the formation of Zeolite A4 from kaolin. *clay minerals* **1996**, 31, 253-261.
6. Stoch, L., Iron in Kaolins; Mineralogical, crystallo-chemical and technological aspects. *Interceramics* **1987**, 6, 21-25.