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Investigations on Selected Indian Kaolins for their Possible Value Addition

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Abstract

Kaolins from Kerala, Orissa, Rajasthan and West Bengal states (designated as KK, OK, RK and WK respectively) were studied for their possible value addition. Size classification followed by physical, chemical and mineralogical characterization of the ROM clays and various size fractions were carried out. All the four samples are found to be kaolinitic with quartz as the major impurity. Small quantity of mica is present in RK and WK whereas pyrite is found in OK. Size classification increases the % of <2μm particles and kaolinite content. Conventional hydros bleaching improved the optical properties only marginally whereas dithionite-citrate-bicarbonate (DCB) treatment considerably enhanced the same. Significant reduction in Fe content and improvement in optical properties on DCB treatment indicate the presence of "free iron" as oxides, hydroxides, sulphides etc. in KK, OK and WK where as in RK iron is "structural", in kaolinite and / or in the micaceous mineral. The investigation shows that even after size classification, impurity minerals remain in the products indicating their ultra fine size. Hence, value addition is possible (more in KK, OK and WK and less in RK) by removing the iron impurities using special techniques such as high gradient magnetic separation, ultra flotation etc. Selected samples were calcined at 1100°C and the optical properties of the calcined samples did not show much improvement.

Keywords: *Kaolin, iron-minerals, dithionite-citrate-bicarbonate, optical properties, beneficiation, value addition*

INTRODUCTION

Kaolin or china clay is one of the most versatile industrial minerals abundantly available in our country and has wide range of applications. The major mineral in china clay is kaolinite. The common ancillary minerals are quartz, titanoferrous, ferruginous, micaceous and carbonaceous impurities which adversely affect its properties. Characterization followed by beneficiation not only prevents the underutilization but also gives value addition to the mineral. Extensive research has been carried out on the nature of iron impurities in kaolin, which concludes that iron may be present in the kaolinite or ancillary mineral structure ie., "structural" or as separate oxides, hydroxides, sulphides etc ie., "free" (Jepson, 1988).

Kaolin finds extensive applications in a variety of industries such as paper, paint, rubber, ceramics, plastics etc. The versatility of kaolin in its applications is due to its unique properties (Murray etal, 1993). One of the highest value additions achieved is in its application as white pigment in paper and paint industries and it has got stringent specifications with respect to particle size distribution and brightness. Stoch et al have discussed the mineralogical, cystallo-chemical and technological aspects of iron impurities in kaolin (Stoch, 1987). The impurities which affect the brightness of kaolin are the colored minerals of iron (Jepson, 1988). Identification of these impurity minerals is essential for selecting and sequentialising the beneficiation techniques for their removal.

The size classification produces different grades of kaolin with varying particle size distribution. Increase in the finer fraction can result in improved brightness due to the increase in surface area and hence more light scattering sites. During sizing, coarser (quartz) and / or denser (ilmenite, rutile etc.) impurity minerals get separated. Even small quantities of the coloring impurities in the finer fractions contaminate the clay and reduce its brightness. Hence, these impurities can be removed only by special techniques such as froth flotation, magnetic separation, oxidative/ reductive bleaching etc. depending upon the nature and quantity of impurities (Murray et al, 1993; Jepson, 1988). The 'calcined' clays have better optical properties, but require milling for achieving the specified particle size Stoch, 1987; Chandrasekhar, 2002).

The present study deals with the investigation on four kaolins from the states of Kerala, Orissa, Rajasthan and West Bengal for their possible value addition.

EXPERIMENTAL

Bulk samples of kaolins were collected from the districts, Kasargod of Kerala (KK), Koraput of Orissa (OK), Pali of Rajasthan (RK) and Bankura of West Bengal (WK). Representative samples were prepared by thorough blending and coning – quartering. Nearly 100 Kg. samples were blunged with water and screened through 300 µm BSS Sieve. The –300 µm fraction slurry was size classified using a set of Mozley hydrocyclones (H/C) viz., 2" stub, 2" standard and 1" cyclones. In the case of sample 'OK', the blunging before screening at 300 µm was replaced with water washing followed by soft mixing. The 2" stub H/C overflow solids (SCP1) correspond to the fraction below 45 µm and the overflow solids of 1"H/C is the final size classified product (SCP2). SCP1 samples were calcined and SCP2 samples were subjected to conventional reductive bleaching as well as DCB treatment (Mehra and Jackson, 1960). All the above operations were carried out at conditions optimized in the laboratory.

The physical, chemical and mineralogical properties were determined by standard methods and the rational analysis data was generated by calculating the mineral percentages from the chemical assay (Bennet and Reed, 1971, Searle and Grimshaw, 1960). XRD analysis was carried out using X-ray diffractometer X'pert Pro, PANalytical (with Cu **kα** radiation using Ni as filter at a setting of 40 kV and 30 mA) and thermal analysis (DTA/TGA) using Thermal analyzer Model Seiko 320 using α-Al_2O_3 as reference material and in air atmosphere. Optical properties were measured by Color Touch spectrophotometer, ISO model, Technidyne Corporation, US and the particle size distribution by Sedigraph 5100 model, Micromeritics, US.

RESULTS AND DISCUSSION

The clay samples under investigation are found to be colored [KK-pink, OK and RK-gray and WK-dull yellow] indicating the association of colored minerals. Properties of the ROM clays show that they are of poor quality and need beneficiation. The detailed characterization studies were conducted on the ROM and beneficiated clays to understand their properties and to explore the possibility of beneficiation to get value added products.

pH

The ROM clays are almost neutral in pH (KK-5.21, RK-7.0 and WK-7.55 units) except OK which is found to be acidic (pH 1.74). The low pH value can be attributed to the presence of pyrite as discussed later. Though pyrite is stable under reduced conditions, lowering of water tables causes pyrite to oxidize, leading to the formation of H_2SO_4 follows.

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{+2} + 2SO_4^{2-} + 2H^+$$

$Fe^{+2} + \frac{1}{4} O_2 + H^+ \leftarrow\!\!> Fe^{+3} + \frac{1}{2} H_2O$

$FeS_2 + 14\ Fe^{+3} + 8\ H_2O \rightarrow 15\ Fe^{+2} + 2SO_4^{\ 2-} + 16H^+$

The formation of acid decreases the pH to a great extent and the concentration of free hydrogen ions in solution cause changes in the speciation of Al and the solubility of toxic metal ions is increased [Zhang etal 1991a,b; Yu, 1997; Mao-Xu-Zhu, 2005]. These changes in soil have important environmental implications.

The acidity of the clay creates problems during wet processing. The soluble iron gets precipitated on dilution because of the subsequent increase in pH. Hence, a water wash was given to the OK clay before size classification. It needs special mention that the acidity of this pyritic clay causes acid mine draining in the mine area which results in the environmental pollution.

Specific Gravity

Specific gravity of the ROM samples of KK, RK and WK are found to be 2.55, 2.61 and 2.63 g/cc respectively, which are very close to that of pure china clay (2.6 g/cc). But the value for OK is slightly higher (2.73) which is due to the presence of pyrite (~5.1). However, the size classified products of OK have values nearer to that of kaolinite indicating the removal of pyrite during this operation.

Matter Soluble in Water / Dil.HCL

The ROM clays except OK are found to have low water solubles (0.30, 0.53 & 1.28 % respectively for KK, RK and WK). After sizing, the values come down to a great extent in the products (ave. value 0.25 %). In OK, water solubles is higher (4.14%) and after sizing it comes down to 0.52%. The reason for this high value can be attributed to mobilization of metals from the clay by H_2SO_4 formed during the oxidation of pyrite. A similar trend is observed for the acid solubles of these samples also. Size classification brings down the value from ~1.75 to 0.6% except for OK where the reduction is from 9.06 to 1.07%. The high value can be due to the presence of other solubles like siderite ($CaCO_3$) in addition to the sulphides.

Particle Size Distribution

The particle size distribution of the ROM clays and products of size classification are given in **Table 1**. In 'KK and WK', the grit content (+ 45μm fraction) in the ROM clay is 36.80 and 43.09 % respectively. After hydrocycloning, recovery of the fraction < 2 μm in the product clays is found to be less and it does not match with the specifications for ceramic or filler grade clays. The grit content of OK ROM clay is ~17% indicating a good recovery during wet processing. The percentage of fraction < 2 μm in both the product clays fall in the range acceptable for ceramic and filler applications. RK sample has negligible grit (0.4%) and has very narrow size distribution, indicating the possibility of good recovery during wet processing. The percentage fraction < 2 μm in the final product clay almost matches with the specifications for the pigment grade clay.

Chemical Analysis

The chemical assay of various samples is given in **Table 2**. The ROM samples of KK, RK and WK are have relatively high SiO_2 content and low LOI values. The kaolinite content in samples KK and RK is higher than that in WK as indicated by the increased Al_2O_3 content. The LOI of OK is high which is due to the presence of pyrite in the sample. Samples OK and WK contain more Fe_2O_3 than the other two samples. Out of the four samples, OK has the highest TiO_2 content. After processing, all the samples except WK become rich in kaolinite. The SCP2 of samples KK, RK and OK contain much less impurities of Fe and Ti and are highly kaolinitic as indicated by the increased Al_2O_3 content. The LOI is also less and near to that of pure kaolinite mineral. It is evident that a reasonable quantity of impurities is getting removed from samples KK, RK and OK during size classification. The SCP2 of sample WK is found to be less kaolinitic as indicated by the high SiO_2 and low Al_2O_3 &

LOI values. Interestingly, the product samples are found to contain more Fe_2O_3 than the ROM clay indicating the ultra fine size of the 'Fe' impurities which are getting enriched in the product during size separation.

Table 1: Particle Size Distribution of ROM and Beneficiated Samples

Clay samples	Particle size distribution (µm, wt. %)	Samples		
		ROM	SCP1	SCP2
KK	>45	36.80	Nil	Nil
	< 45 > 20	1.45	3.00	Nil
	< 20 > 10	5.35	7.00	Nil
	< 10 > 5	11.96	17.70	9.30
	< 5 > 2	17.61	26.60	31.40
	< 2	26.83	45.70	59.30
OK	>45	16.80	Nil	Nil
	< 45 > 20	4.70	8.20	1.40
	< 20 > 10	5.80	5.70	3.70
	< 10 > 5	8.80	9.30	7.40
	< 5 > 2	14.00	15.70	13.60
	< 2	49.90	61.10	73.90
RK	>45	0.40	Nil	Nil
	< 45 > 20	0.00	0.70	Nil
	< 20 > 10	4.60	4.30	Nil
	< 10 > 5	6.40	5.70	3.60
	< 5 > 2	15.90	13.60	13.10
	< 2	72.70	75.70	83.30
WK	>45	43.09	Nil	Nil
	< 45 > 20	5.23	7.72	Nil
	< 20 > 10	8.65	14.41	Nil
	< 10 > 5	12.46	15.56	5.60
	< 5 > 2	10.47	19.89	38.64
	< 2	20.10	42.42	55.76

Table 2: Chemical Assay and Mineralogy of ROM and Beneficiated Samples

Clays	Samples	Chemical assay (% by weight)								Minerals (from XRD)
		SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	K_2O	CaO	LOI	
KK	ROM	51.93	36.90	1.06	0.57	0.20	0.41	0.13	8.39	Q, K
	SCP1	45.26	37.78	1.07	0.49	0.10	0.22	0.06	14.27	K, Q
	SCP2	46.96	36.18	1.07	0.41	0.32	0.20	0.20	14.53	K, Q
OK	ROM	41.81	32.01	5.41	1.60	0.23	0.08	0.69	18.17	K, Q, P
	SCP1	42.47	37.71	2.05	0.80	0.20	0.08	0.58	17.12	K, Q
	SCP2	41.92	38.91	1.16	0.66	0.23	0.02	0.69	15.98	K, Q
RK	ROM	52.52	33.04	1.10	0.52	0.33	0.56	0.34	11.79	Q, K
	SCP1	48.55	34.18	1.13	0.62	0.33	0.70	0.45	13.23	K, Q, M
	SCP2	46.17	35.66	1.04	0.55	0.37	0.62	0.51	14.30	K, Q, M
WK	ROM	73.54	16.40	3.94	0.44	0.28	1.25	0.90	4.66	Q, K, M
	SCP1	53.85	26.60	5.17	0.77	0.33	3.05	2.31	7.77	Q, K, M
	SCP2	49.76	30.01	5.66	0.28	0.48	2.76	1.93	9.84	Q, K, M

K -Kaolinite; Q -Quartz; P –Pyrite; M– Mica

Mineralogical Studies

X-ray diffraction, thermal and rational analyses give an overall picture of the clay mineralogy. **Figure 1** represents the XRD powder patterns of the ROM samples. Kaolinite is found to be the major mineral and quartz is also present in all the four samples. Peaks of mica are observed in the patterns of RK and WK and those of pyrite in sample OK. The impurities are present in varying amounts in the ROM and processed samples. It is seen that after processing, the kaolinite content in all the four samples has increased. However, the product samples of WK were found to contain appreciable amount of quartz. The rational analysis data also supports the same. **Table 2** gives the mineralogy of the samples.

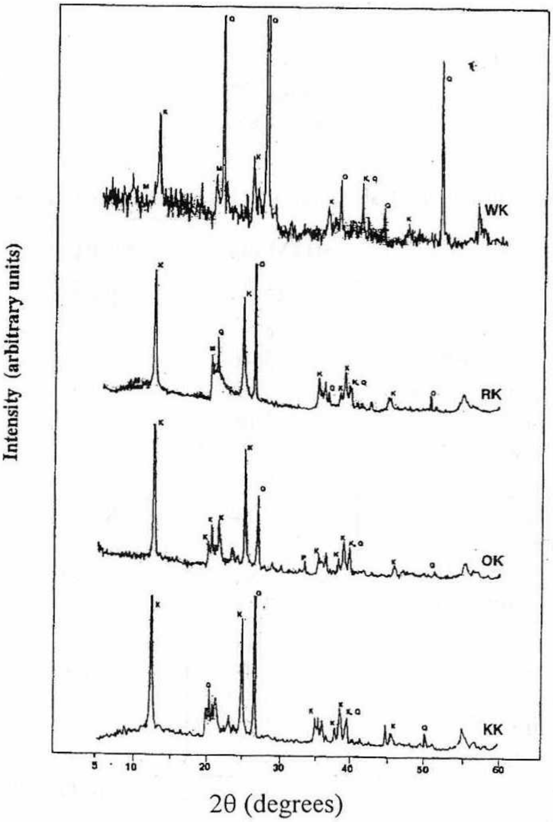

Fig. 1: XRD Patterns of ROM Samples
K - Kaolinite; Q - Quartz; P - Pyrite; M - Mica

Thermal analyses (TGA & DTA) indicate the change in weight and structural changes on heating the samples to 1000°C. The ROM, SCP1 and SCP2 samples of all the clays show DTA patterns characteristic of kaolinite mineral [endotherm at ~560°C and exotherm at ~980°C]. Pyrite under oxidative conditions undergoes exothermal transformation to hematite which occurs in several steps between 440 and 540°C. The ROM and SCP1 of OK show exotherms at 468 and 439°C respectively indicating the significant amount of pyrite in these samples. The SCP2 of all the four samples are found to be highly kaolinitic and only the endotherm and exotherm of kaolinite mineral are observed in their DTA patterns. TGA analysis shows that all the ROM samples except OK have low weight losses, which can be due to the low kaolinite content. After processing, the weight loss of the products increases almost to that of typical kaolinite. The ROM of OK shows weight loss of ~18.3 % due to

Table 3: Thermal Analysis Data of ROM and Beneficiated Samples

Clay	Samples	TG (wt. loss %)	DTA (°C)	
			Endotherm	Exotherm
KK	ROM	9.46	527.5	995.3
	SCP1	12.41	532.1	993.0
	SCP2	13.13	532.7	994.7
OK	ROM	18.27	534.3, 684.9, 73.4	468.0, 554.8, 983.8
	SCP1	16.49	534.4, 671.3	438.5, 981.6
	SCP2	16.20	563.8, 671.6	695.5, 749.1, 992.2
RK	ROM	13.76	547.1, 75.5	975.6
	SCP1	13.23	547.1, 75.5	978.0
	SCP2	14.04	547.1, 73.2	975.5
WK	ROM	5.02	575.8, 532.7, 85.1	975.6
	SCP1	6.21	532.7, 85.1	975.6
	SCP2	13.56	525.2, 73.4	963.3, 717.0

Table 4: Rational Analysis Data of ROM and Beneficiated Samples

Clay sample	Mineral % by wt.	ROM clay	SCP1	SCP2
KK	Kaolinite	87.54	85.95	92.61
	Quartz	8.46	4.34	0.76
	Muscovite Mica	3.46	1.70	1.88
	Paragonite Mica	2.51	3.97	1.24
	Hematite	1.06	1.07	0.80
	Anatase	0.57	0.41	0.49
	Calcite	0.23	0.11	0.12
OK	Kaolinite	77.54	88.99	87.09
	Quartz	4.10	0.69	---
	Muscovite Mica	0.68	2.48	0.17
	Paragonite Mica	2.84	0.65	2.84
	Pyrite	1.92	1.83	0.31
	Hematite	4.14	0.80	0.95
	Anatase	1.60	1.04	0.66
	Calcite	1.78	1.32	1.23
	Free alumina	---	---	3.32
RK	Kaolinite	74.98	76.77	80.56
	Quartz	13.60	8.29	4.16
	Muscovite Mica	4.75	5.90	5.24
	Paragonite Mica	4.03	4.01	4.60
	Hematite	1.10	1.13	1.04
	Anatase	0.52	0.62	0.55
	Calcite	0.61	0.79	0.91
WK	Kaolinite	27.74	38.15	47.31
	Quartz	54.22	22.52	14.41
	Muscovite Mica	10.58	25.80	23.35
	Paragonite Mica	3.45	4.06	5.89
	Hematite	3.94	5.17	5.66
	Anatase	0.44	0.78	0.28
	Calcite	1.61	4.12	3.78

the presence of pyrite. After processing, it comes down to ~ 16.2 % indicating that majority of the pyrite particles are getting removed during size separation. **Table 3** gives the thermal analysis data of various samples.

Rational analysis of ROM, SCP1 and SCP2 calculated from the chemical assay also gives their probable mineralogy as given in **Table 4.** However, it is to be remembered that the mineral content has been calculated from the chemical assay based on some assumptions and hence the method is just "rational". These so-called proximate analyses (calculated mineralogical compositions) can provide sufficiently adequate picture for most practical purposes.

Table 5: Optical Properties and Fe & Ti Content in the ROM and Beneficiated Samples

Clay sample	Samples	Fe_2O_3 %	TiO_2 %	B	L	a	b	HW	HY
KK	ROM clay	1.06	0.58	60.51	80.12	2.60	3.30	49.08	5.89
	SCP1	1.07	0.49	66.65	85.03	3.03	4.73	49.33	7.94
	SCP2	1.07	0.41	66.56	85.66	3.33	4.83	49.74	8.05
	SCP1 after	ND	ND-	69.07	85.41	1.54	3.25	57.09	5.43
	calcination	0.95	0.41	68.12	85.74	3.14	4.47	51.60	7.45
	SCP2 after reductive								
	bleaching	0.61	0.34	83.27	92.72	-0.36	2.15	74.59	3.31
	SCP2 after DCBT								
OK	ROM clay	5.41	1.60	45.87	67.43	-0.75	-0.44	47.17	-0.94
	SCP1	2.05	0.80	68.13	88.21	-0.86	7.91	37.95	12.81
	SCP2	1.16	0.66	70.45	88.92	-0.89	7.02	43.41	11.27
	SCP1 after	ND	ND	65.58	83.46	2.65	3.45	53.23	5.97
	calcination	0.93	0.66	73.32	89.31	-0.47	5.22	53.10	8.36
	SCP2 after reductive								
	bleaching	0.50	0.66	83.41	92.41	-0.31	1.58	77.06	2.44
	SCP2 after DCBT								
RK	ROM clay	1.10	0.52	80.16	93.01	-0.50	4.98	60.02	7.65
	SCP1	1.13	0.62	79.97	92.65	-0.44	4.50	61.86	6.95
	SCP2	1.04	0.55	80.08	93.06	-0.38	5.12	59.34	7.87
	SCP1 after	ND	ND	76.36	89.[illegible]1	-0.24	2.46	66.86	3.95
	calcination	1.02	0.55	80.59	93.12	-0.44	4.80	61.16	7.37
	SCP2 after reductive								
	bleaching	1.00	0.49	81.10	92.50	-0.43	3.56	66.77	5.49
	SCP2 after DCBT								
WK	ROM clay	3.94	0.44	37.69	74.29	0.07	16.77	16.01	32.25
	SCP1	5.17	0.77	41.48	80.14	0.65	20.15	28.01	35.92
	SCP2	5.66	0.28	41.79	81.09	1.07	20.99	31.50	36.98
	SCP1after	ND	ND	ND	ND	ND	ND	ND	ND
	calcination								
	SCP2 after reductive	4.86	0.28	46.45	84.67	1.25	22.72	33.04	38.19
	bleaching	0.94	0.28	69.67	86.16	-1.32	4.03	54.41	6.68
	SCP2 after DCBT								

ND – Not Determined

Optical Properties

Optical properties, % Fe_2O_3 and % TiO_2 values of ROM and beneficiated samples are given in **Table 5**. For pigment grade kaolin, brightness should be >80% ISO and beneficiation to achieve this level is one of the highest value additions of kaolin. Size classification increases the brightness of SCP2 samples ie., by 25.5 (OK), 6.0(KK) and 4.0 (WK) units. However, it failed to make any improvement in RK. Coarse and colored impurity minerals are getting removed during size classification improving brightness. The high improvement in brightness of sample 'OK' during size separation is due to the removal of the pyrite which is mostly coarser in size and dark in color. The reduction in the Fe_2O_3 content of the samples SCP1 and SCP2 also supports the same.

It is interesting to see that SCP1samples of the clays have responded differently to calcination. In the case of calcined KK there is a marked improvement, ~6.0 units, in the brightness, increase in the 'L' and decrease in 'a' values. On the other hand, brightness of samples RK and OK has decreased on calcination. The structure of kaolinite and other minerals breaks down and the iron gets liberated and oxidized to give the colored oxides thus reducing the brightness. The increase in the 'a' value (indicative of free iron) also supports the same. Calcination of the sample WK was not done due to the very poor optical properties of the sample.

With respect to chemical leaching, the term "structural iron" has been used for the iron substituted in the structure of kaolinite as well as the ancillary minerals like pyrite, anatase, mica etc. which are not easily leachable. The DCB method (Mehra and Jackson, 1960) removes the free iron oxides with a minimal effect on the crystalline clay and this extractable iron is a fair estimate of pedogenic iron oxides in soils and kaolins (Ole K.Borgaard, 1988).It is reported that DCB treatment releases large amount of Fe from the gray clay (Schroeder et al., 2004). The reduced "S" species in DCB solutions, releases Fe selectively from fine grained pyrite (Canfield et al., 1992).

The conventional reductive ('hydros') bleaching removes only very small amount of 'Fe' minerals. Hence, the brightness improvement of the product sample SCP2 is also marginal. The brightness of KK, OK, RK & WK has improved on hydros bleaching by ~ 1.5, 3.0, 0.5 and 4.5 units respectively with marginal reduction in the Fe_2O_3 content. DCB treatment is more powerful due to the severe experimental conditions and a maximum removal of free iron is achieved. For all the samples, the brightness improvement is almost same for 2nd and 3rd DCB treatments. So the SCP2 samples subjected to two successive DCB treatments was taken as the sample for the present study. Out of the four samples, OK and WK contain more Fe_2O_3 and have inferior optical properties. DCB treatment improves the brightness of OK by ~13.0 units with a decrease in % Fe_2O_3 from 1.16 to 0.50 and brightness of WK by ~ 28.0 units with a decrease in % Fe_2O_3 value from 5.66 to 0.94 respectively. When subjected to DCB treatment, KK also gives a sharp increase in brightness (~17 units) with a decrease in % Fe_2O_3 value from 1.07 to 0.61. This indicates that most of the iron in KK, OK and WK is "free" and leachable. But DCB treatment of RK produces only marginal improvement of 1 unit in brightness with negligible reduction in Fe_2O_3 content. This clearly shows that the iron mineral present in RK is 'not free' and hence not leachable. The "Fe" may be present as part of the kaolinite and / or mica structure.

The brightness/whiteness of kaolin is dependent on the overall effect of the ***Lab*** colour values. It has been established that the "free iron" is more soluble than the "structural" iron and hence the former is more easily removed by chemical leaching. The "***L***" values of RK, OK and WK increase after DCB treatment to a greater extent than that of RK. The ***a*** & ***b*** values can be directly correlated to the "free" and "structural" iron respectively. After DCB treatment "***a***" values (reddishness) of samples KK, OK and WK have come down by ~3.5, 0.5 and 2.5 units respectively. This indicates that samples "KK and WK contains more free iron than OK. But in the case of sample RK there is no change in the 'a" value after DCB treatment indicating that it contains no "free iron". The "b" values (yellowness) were found to decrease, 2.7 in KK, 5.5 in OK, 1.7 in RK and 17 in WK on DCB treatment. The removal of micaceous iron in WK and pyritic iron in OK is contributing to the substantial decrease in yellowness.

CONCLUSIONS

All the four clay samples are kaolinitic and quartz is the major impurity along with mica in samples from Rajasthan and West Bengal and pyrite in Orissa clay. Kerala and West Bengal clays contain relatively high amount of quartz. The response of the clays to DCB treatment confirms that in Kerala and Orissa clays iron is present in the form of "free" minerals such as oxides, hydroxide, sulphides etc., where as in Rajasthan and West Bengal samples, the same is present as part of the structure of kaolinite and / or mica. The investigation shows that even after size classification, all the kaolin samples contain impurity minerals in the ultrafine size ranges. Hence, higher value addition can be achieved only by removing these ultra fine colored impurities using special beneficiation techniques such as high gradient magnetic separation, ultra flotation etc.

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