

Chemical, mineralogical and morphological characterisation of kaolinitic clays

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ABSTRACT

Kaolin is one of the most important white minerals which has got applications in a variety of industries. The nature of kaolin and the ancillary mineral contaminants depend upon (i) the genesis / origin of the mineral ie., from feldspathic or micaceous rocks, and (ii) the nature of the deposit ie., primary, secondary or hydro-thermal. The present investigation is on a kaolin sample from India and another from Germany. A systematic study on physical, chemical and mineralogical characterisation showed that both the clays are highly kaolinitic, but the ancillary mineral contaminants are different. The German clay is already being processed for various applications whereas the optimal utilisation of the Indian clay is under study. The trace elements in the clays were also estimated to get some idea about the genesis of the clay. Iron containing titania was found to be the major colouring impurity in the Indian clay while orthoclase feldspar, mica and quartz were found in the German clay. Attempts were also made to find out whether the iron in the clay is "free" or "structural". The poor response to citrate-dithionite-bicarbonate dissolution method indicated that most of the iron in both the clays is structural. The magnetic fraction separated from the Indian clay was also characterised for identifying the mineral impurities. X-ray Diffraction, Thermal Analysis, Electron Microscopy and Chemical Analysis studies substantiated the findings.

Key words : Kaolin, Beneficiation, Ancillary minerals, Characterisation, Genesis

INTRODUCTION

The wide industrial applications of kaolin or china clay are essentially due to its unique properties^[1]. India has got vast deposits of this mineral mainly spread in the states of West Bengal, Rajasthan, Bihar, Gujarat, Kerala, Orissa, Karnataka and Tamil Nadu. The recoverable reserves is around 986 million tons and the total production is comparatively low^[2] ie., only 7.7 lakh tons during 1994-95.

Modern techniques for achieving the required stringent specifications for kaolin in paint, paper, rubber, plastics, special ceramics etc. are still alien to India, the important reasons being the difficulty in the speciation of impurity minerals and lack of technical knowledge. This results in the underutilisation of this non-replenishable resource.

Kaolin contains "kaolinite" as the major mineral which is hydrous aluminium silicate $[\text{Al}_2\text{Si}_2(\text{OH})_4]$ made up of alternate octahedral gibbsite and tetrahedral silica layers. These basic building blocks of the lattice do not absorb light in the visible range (350-800nm). Absorption in this region results from the presence of transition metal cations the most important being iron^[3]. The nature of electronic transitions associated with light absorption can be either "intraconfigurational" or "charge transfer". The former refers to transitions between levels belonging to the same electronic configuration whereas the latter is due to partial migration of an electron from one nuclear centre to another. In kaolins charge transfer is generally found. The colouring impurities generally present in kaolin are ferruginous, titaniferous, micaceous and carbonaceous minerals and beneficiation of kaolin for removing these impurities is essential for most of its applications. Quartz which is generally coarse in size is easily removed during size classification. The coloured minerals affect the brightness of kaolin and sometimes remain uniformly distributed in all the size fractions. Modern beneficiation methods such as High Gradient Magnetic Separation (HGMS), Ultra-flotation, Selective Flocculation, Chemical Leaching etc. are to be adopted for the removal of the ancillary minerals especially in the ultrafine size range.

The present paper deals with the characterisation of two kaolins of different origin i.e., one from India and the other from Germany. The intermediates and products during the size classification and the magnetically separated ferruginous impurities from the Indian clay are also studied.

EXPERIMENTAL

Sample Selection

Bulk quantities of the Indian china clay was collected and size classified to get products and intermediates of varying particle size distribution. The ROM clay, a product containing all particles below 45 μm (Size Classified Clay, SCC) and another with nearly 90% particles below 2 μm (Final Size Classified Product, FSCP) were selected for the study. An unbleached sample of china clay supplied by the Amberger Kaolin Werke, Hirschau, Germany (AKW) was also included. When the mineral impurity content in the clay is small, the identification becomes very difficult and a concentration step is done. Thus the magnetic fraction (Mag) separated from FSCP by Super Conducting High Gradient Magnet (SC HGMS) was also taken for the investigation.

Characterisation

The five selected samples were characterised for their physical, chemical and mineralogical properties by adopting standard methods.

- (i) X-Ray Diffraction (XRD) Philips X-ray diffractometer Model X'Pert was used for the understanding the mineralogy of the clays.
- (ii) Thermal Analysis of the samples was done by DTA / TGA Model Seiko 320.
- (iii) Electron microscopic studies were done using an SEM (Model Philips) with EDS attachment and TEM (Model Philips HRTEM CM 200 D 823)
- (iv) Chemical analysis: Standard wet chemical and instrumental methods were adopted for determining the constituents of the clays^[4]. SiO_2 was estimated by gravimetry, Al_2O_3 by indirect complexometry, Fe_2O_3 and TiO_2 by colorimetry and CaO , Na_2O and K_2O by flame photometry. The clay samples were dissolved in a mixture of HCl , HNO_3 and HF by digesting in a High Performance Microwave Digestion Unit mls 1200 mega system and the trace elements were determined using a Perkin Elmer Plasma II Emission Spectrometer.

Citrate-Dithionite-Bicarbonate (CDB) Treatment

Dissolution of iron in a mixture of sodium citrate, dithionite and bicarbonate solutions of definite composition at $75\text{--}80^\circ\text{C}$, at pH 7.3 and separation by filtration followed by washing was carried out on the FSCP and AKW clay samples^[5]. Chemical analysis for Fe_2O_3 and TiO_2 and brightness measurements of the feed and product clays were also done. The sample FSCP was subjected to CDB treatment three times consecutively to get maximum extraction of iron.

RESULTS AND DISCUSSION

The characterisation of the Indian and AKW clays showed that both clays are kaolinitic in nature but contains different types of mineral impurities. The "Mag" sample is also essentially kaolinite with slightly higher percentages of ferruginous and titaniferous minerals.

XRD Analysis

The identification of the crystalline minerals present in the clay has been carried out mainly by this method. Fig.1 gives the XRD patterns of the AKW, ROM, SCC, FSCP and "Mag" samples. Kaolinite is the major phase in all these samples. The AKW clay contains quartz, orthoclase feldspar, rutile and muscovite mica as the minor minerals. The Indian clay has anatase and rutile impurities. The "Mag" fraction is found to contain more rutile and anatase. Trace

amounts of goethite, iron oxide and muscovite mica could also be detected in the "Mag" whereas the XRD of the original clay did not indicate the presence of the same.

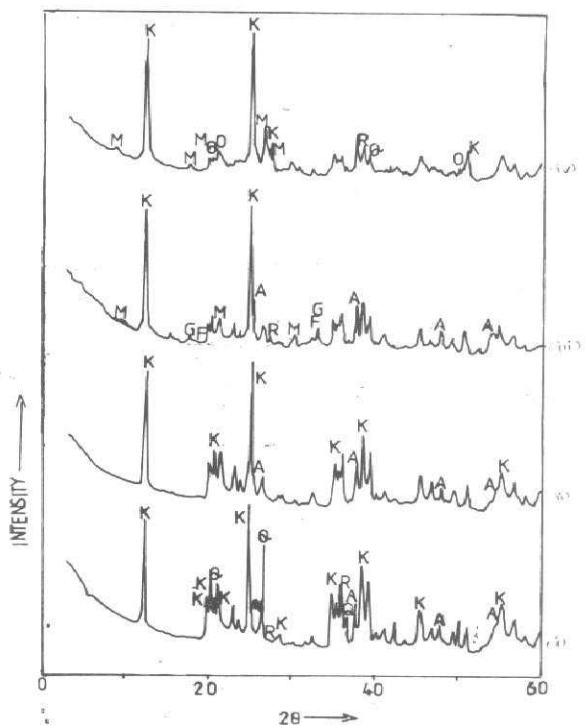


Fig. 1 : XRD patterns of (i) ROM (ii) FSCP (iii) Mag. fraction (iv) AKW clay
A - Anatase; F-Iron oxide; G - Goethite; K - Kaolinite; M - Mica;
O - Orthoclase; Q - Quartz; R - Rutile

Thermal Analysis

The DTA / TG curves of AKW, FSCP and the "Mag" are shown in Fig.2. An endotherm at $\sim 520^{\circ}\text{C}$ corresponding to the loss of structural water and an exotherm at $\sim 985^{\circ}\text{C}$ due to the phase transition (mullite formation) are characteristic of kaolinitic mineral and are observed in all the samples^[6]. The TG curve gives the loss in weight on heating the samples which match with the values obtained by chemical analysis. Even though the "Mag" contains more impurities, the quantity of the same seems to be too low to have any influence on its thermal behaviour.

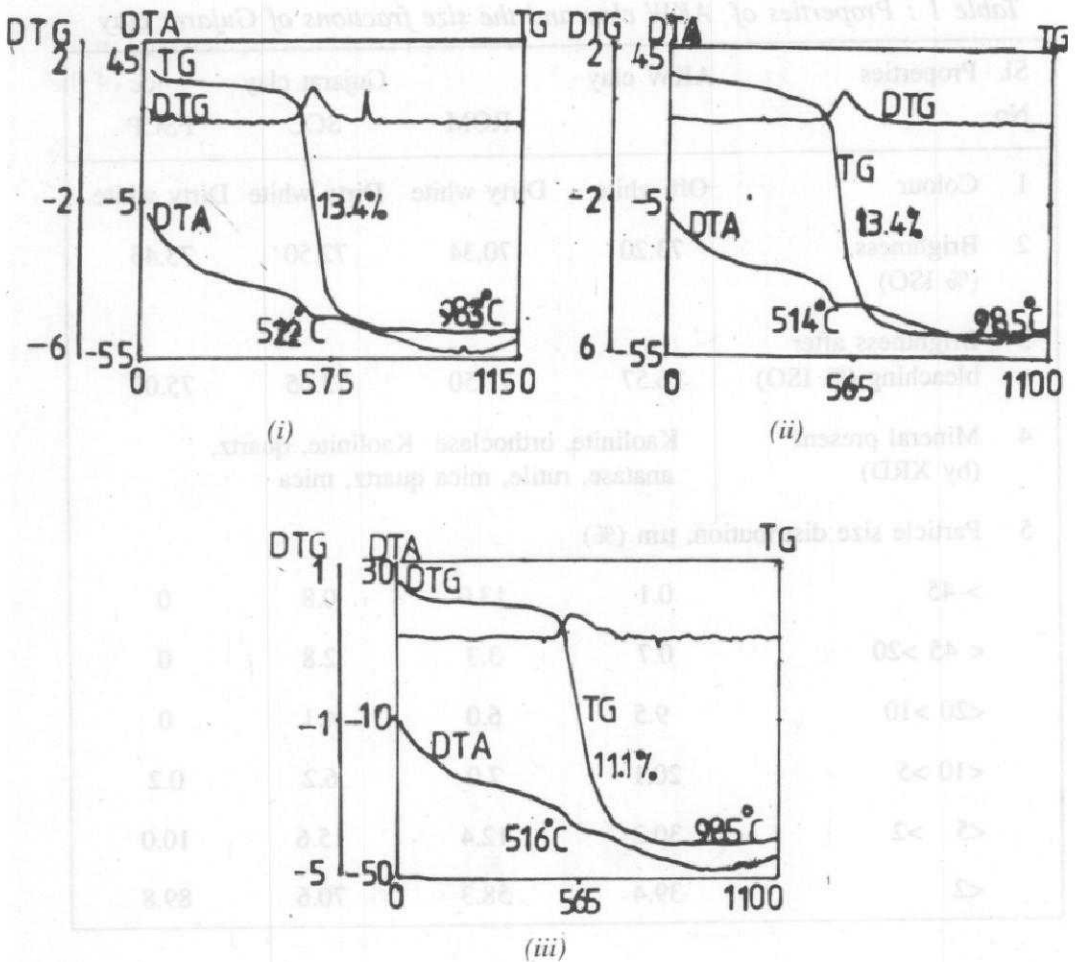


Fig. 2 : DTA/TG Curves of (i) FSCP (ii) Mag. fraction (iii) AKW clay

Particle Size Distribution Analysis

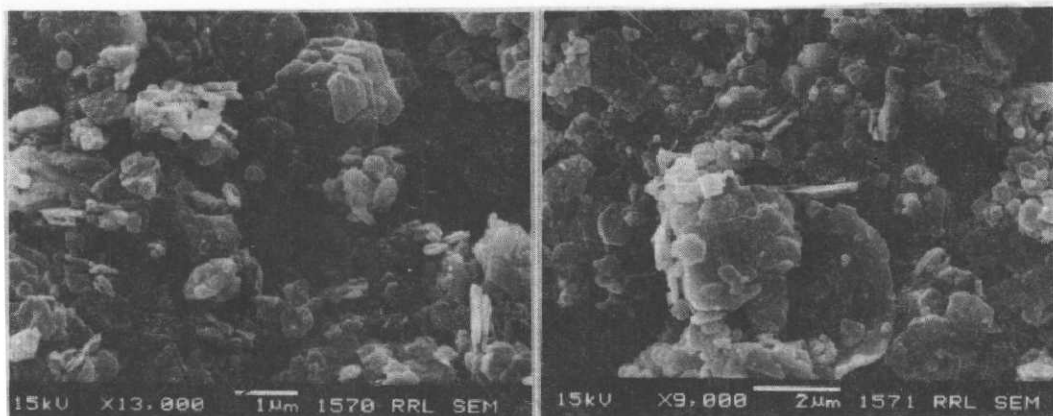
The size distribution of particles and other general properties of the AKW, ROM, SCC and FSCP clays are given in Table 1. The Indian clay contains much higher percentage of fines compared to the AKW clay. The size classification of the former increases the percentage of fines and the FSCP has ~90% particles below 2 μm size. Incidentally, this product matches with the international specification for coating grade clay with respect to the particle size^[1].

Table 1 : Properties of AKW clay and the size fractions of Gujarat clay

Sl. No.	Properties	AKW clay	ROM	Gujarat clay SCC	FSCP
1	Colour	Off white	Dirty white	Dirty white	Dirty white
2	Brightness (% ISO)	73.20	70.34	72.50	73.45
3	Brightness after bleaching (% ISO)	76.57	71.50	73.65	75.00
4	Mineral present (by XRD)	Kaolinite, orthoclase, anatase, rutile, mica			
5	Particle size distribution, μm (%)				
	> 45	0.1	13.0	0.8	0
	< 45 >20	0.7	3.3	2.8	0
	<20 >10	9.5	6.0	4.1	0
	<10 >5	20.1	7.0	6.2	0.2
	<5 >2	30.2	12.4	15.6	10.0
	<2	39.4	58.3	70.6	89.8

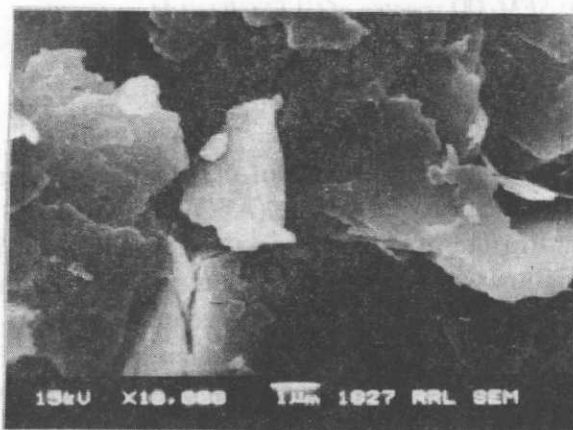
Electron Microscopic Study

The SEM pictures of the FSCP, "Mag" fraction and the AKW clay are given in Fig. 3 and the TEM photographs of the FSCP and Mag" are shown in Fig.4. The hexagonal and pseudo hexagonal crystals of kaolinite are clearly seen in the pictures. It is also observed that even the FSCP contains undisturbed stacks/books of kaolinite platelets. A de lamination process can improve the aspect ratio of the kaolin which has got significance in the paper coating application^[7]. Electron microscope microprobe analysis has been used as a technique for determining the composition of kaolinite by estimating Si and Al at different spots/particles^[8]. The SEM-EDS analysis of the FSCP and the "Mag" fraction has been carried out to determine Fe and Ti. Fig.5 clearly indicates the increase in the concentration of Fe and Ti in the "Mag" sample.



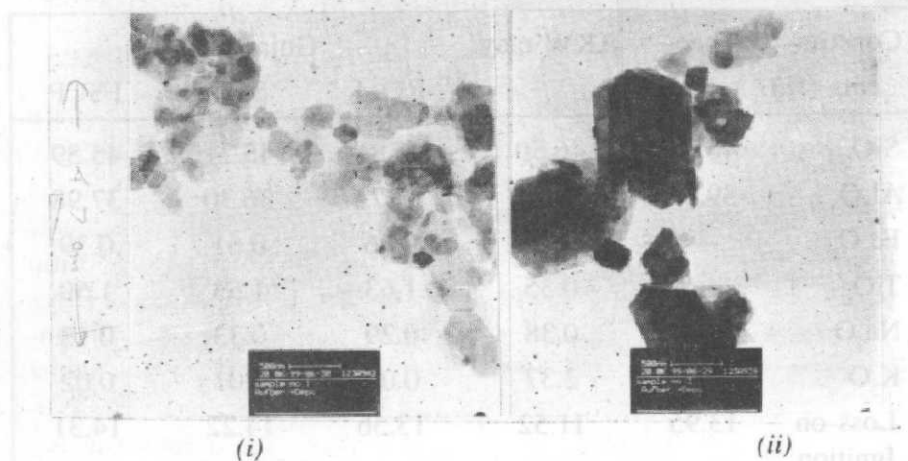
(i)

(ii)



(iii)

Fig. 3 : SEM pictures of (i) FSCP (ii) Mag. fraction (iii) AKW clay



(i)

(ii)

Fig. 4: TEM pictures of (i) FSCP (ii) Mag. fraction

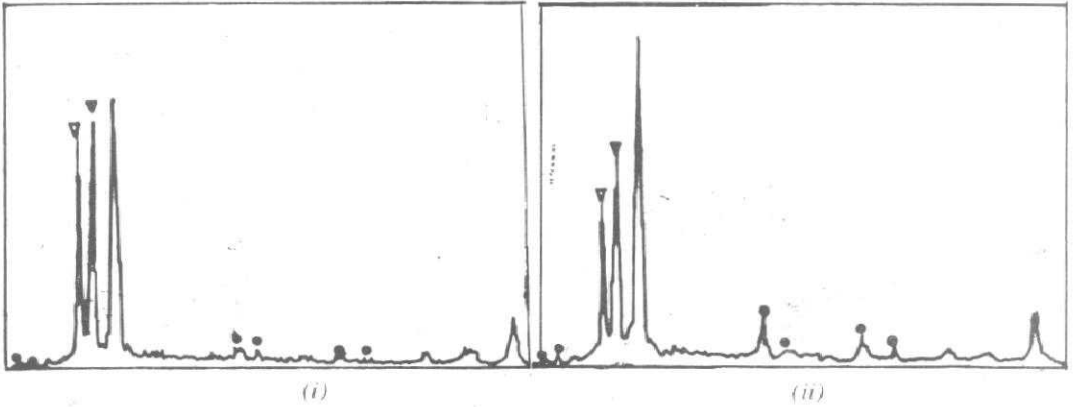


Fig. 5: SEM-ED spectra of (i) FSCP (ii) Mag. fraction
○ - Fe; ● - Ti; ▼ - Al; ▽ - Si

Chemical Assay

The percentage of chemical constituents of the clay samples are closer to the theoretical chemical composition of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). The additional constituents correspond to the ancillary mineral impurities as evident from the Table 2. The low brightness values of the clays are due to the presence of colouring impurities. In the Indian clay, the percentage of TiO_2 is higher. The AKW clay contains low values of TiO_2 slightly higher amount of Fe_2O_3 . The free quartz in the clay is indicated by the higher silica content and lower LOI value. The high potassium content can be attributed to the orthoclase feldspar detected by XRD.

Table 2 : Chemical analysis of AKW clay and the size fractions of Gujrat clay

Sl.No.	Constitu- ents (%)	Theo- retical	AKW clay	Gujarat clay		
				ROM	SCC	FSCP
1	SiO_2	46.51	46.50	45.81	45.21	45.39
2	Al_2O_3	39.54	38.20	37.72	36.30	37.98
3	Fe_2O_3	—	0.49	0.86	0.61	0.39
4	TiO_2	—	0.35	1.63	1.53	1.59
5	Na_2O	—	0.38	0.29	0.33	0.13
6	K_2O	—	2.37	0.03	0.01	0.02
7	Loss on Ignition	13.95	11.52	13.56	14.22	14.31

The properties of the "Mag" sample are given in Table 3. Even though the percentage of iron is not high in the clay, the brightness of the clay is affected to a great extent. The magnetic separation of the impurities has increased the brightness of the clay by about 7% ISO. The "Mag" sample contains almost similar quantities of Fe_2O_3 as well as TiO_2 indicating the both are closely associated.

Table 3 : Properties of the magnetic fraction (Mag) from FSCP

Sl. No.	Properties	
1	Colour	Brown
2	% Fe_2O_3	5.78
3	% TiO_2	8.19
4	Minerals present	Kaolinite, anatase, rutile, goethite, muscovite and iron oxide

In the trace elements analysis, cerium, cadmium and bismuth are not detected in any of the samples. The quantity of other elements in the ROM, SCC and FSCP were found to have only small variation except in the case of zirconium. During size classification, nearly 40% of zirconium was found to be removed in the first stage of classification ($45\mu\text{m}$). Vanadium, zirconium, chromium, nickel, cobalt and titanium contents were found to be higher in the Indian clay whereas AKW clay was richer in lead and zinc. Table 4 gives the results of trace elements analysis in all the clays.

Nature of Iron

Our earlier studies have indicated that the colouring impurity in the Indian clay is "titaniferous" in nature^[9]. The iron containing impurities are known to affect the white colour of kaolin. An attempt was made to find out the amount of free iron i.e., which can be extracted from the clay without disturbing the structure. The CDB treatment is reported to be the most effective method for removing iron from the soils. The FSCP and AKW clays were subjected to CDB treatment and Table 5 gives the percentage of Fe_2O_3 , TiO_2 and the ISO brightness of the feeds and products. It is clearly indicated that only a small portion of the iron is removed even after treating the FSCP three times with CDB. The AKW clay also does not improve much. Thus, it can be inferred that most of the iron in these clays is structural in nature. However, the CDB treatment is not industrially viable due to various reasons such as very high dosage of chemicals, high temperature for the reaction etc. The "hydros" (sodium dithionite) bleaching at pH 2.5-3.0 which is commonly adopted in kaolin beneficiation gave only marginal improvement in brightness for both the clays.

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Table 4 : Trace elements ($\mu\text{g /g}$) in AKW clay and the size fractions of Gujarat clay

Sl.No.	Elements	AKW clay	Gujarat clay		
			ROM	SCC	FSCP
1	Vanadium	3.4	13.9	13.1	13.4
2	Chromium	2.5	15.4	16.2	13.4
3	Manganese	4.1	4.6	2.4	2.2
4	Cobalt	0.7	2.3	2.0	1.9
5	Nickel	n.d	3.2	3.4	3.2
6	Copper	11.1	1.1	1.2	1.3
7	Zinc	4.1	1.5	2.0	2.4
8	Lead	28.0	6.9	8.5	6.2
9	Strontium	1.6	5.3	4.7	5.0
10	Lithium	2.1	7.7	8.7	8.6
11	Zirconium	17.3	63.0	45.2	37.9
12	Cerium	n.d	n.d	n.d	n.d
13	Cadmium	n.d	n.d	n.d	n.d
14	Bismuth	n.d	n.d	n.d	n.d
n.d - Not detected					

Table 5 : Iron and titanium (%) in the clays before and after CDB treatment

Sl.No.	Sample details	% Fe_2O_3	% TiO_2	Brightness (% ISO)
1	FSCP as such	0.39	1.60	73.45
	One treatment	0.34	1.55	76.20
	Two treatments	0.33	1.49	76.65
	Three treatments	0.32	1.48	77.13
	AKW clay	0.49	0.35	73.20
	One treatment	0.42	0.31	76.57

Iron minerals are the most common colouring impurity found in kaolin. Iron can be present as discrete iron compounds such as oxides, hydroxide, hydroxy oxide, carbonate, sulphide etc. ie., free. It can also be present as isomorphous substitution in minerals like kaolinite, mica, rutile, anatase etc. ie., structural^[10,11]. The nature of titania in kaolin has been studied in detail by Weaver^[12]. Even though pure titania is one of the best white pigments, ferruginous titania is coloured and affect the brightness of clays, however small the iron percentage may be. The Fe apparently accounts for the weak magnetic properties of the anatase that allow some of it to be removed by a strong magnet. It has been reported that substitution of Ti by FeIII is is typical for pedogenic anatases as compared to hydrothermal or other lithogenic ones. During the weathering of Ti bearing Fe rich silicates like biotites and pyroboles, an ample supply of Fe is found in the weathering conditions and FeIII enters the tetragonal structure of anatase in measurable amounts. The XRD peak of such compounds matches with that of anatase and the peak becomes broader as the Fe content increases^[13]. The $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$ charge transfer processes and the "Ti - effect" on the broadening and intensification of $\text{O}^{2-} \rightarrow \text{Fe}^{2+}$ bands so that they encroach on the visible region influencing the colour are explained by Faye et al^[14]. Iron compounds can also be present as "stains" on other minerals. The "free" iron mostly responds to chemical leaching or bleaching whereas "structural" iron does not. The latter type of impurities can be removed by physical (magnetic) or physico-chemical (flotation) methods. Super conducting High Gradient Magnetic separation has been an established technique in the well known china clay beneficiation plants at Georgia (US), Brazil, AKW (Germany), Cornwall (UK) etc. Froth flotation is also used in certain plants depending upon the nature of the impurities.

Kaolinite of hydrothermal origin and that formed by weathering of feldspar and muscovite in granitic and pegmatitic rocks generally have a low iron and titanium content. The quartz content is generally higher which results in the low recovery of clay from these deposits. The well known Cornwall (UK) and Brazilian deposits belong to this category and the AKW clay is also found to be similar in nature. The kaolin deposits derived from biotite rich granites, granite gneiss and schists such as those in Georgia (US) have relatively high titanium content because the dark minerals like ilmenite, rutile, biotite, garnet etc. contain titanium abundantly along with elements like vanadium, chromium, nickel, cobalt etc. The genesis of the Indian clay also seems to be similar as indicated by the properties. Depending upon the origin of kaolinite, the nature of ancillary minerals differ and the processing methods for value addition have to be selected accordingly.

CONCLUSION

1. Studies were conducted on a kaolin from India which is yet to be processed for its optimal applications and also on a clay from Germany which is already processed for a variety of applications. Both the clays were found to be highly kaolinitic in nature.
2. Iron containing titania is found to be the major ancillary mineral impurity in the Indian clay whereas orthoclase feldspar and mica contribute to the major mineral impurities in AKW clay.
3. The size classification of the ROM clay from India gives a final product containing ~90% particles < 2 μ m. The impurity minerals like quartz and zircon are removed during this process whereas titaniferous minerals are almost uniformly distributed in the clay.
4. Most of the iron in both the clays is "structural" in nature which is indicated by their poor response to chemical bleaching. Hence, physical (SC HGMS) and physico-chemical (froth flotation) methods are more suitable for the removal of the same.
5. The undisturbed stacks / books in the final size classified Indian clay indicate that de lamination process can improve the product clay quality by increasing the aspect ratio of the sample.

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INTRODUCTION

Characterization of coal is considered to be one of the important steps that would provide great information in utilization point of view. Petrographic characterization of coal is extensively used in coke-making industry particularly to assess the reactivity of coals for combustion and liquefaction etc. The petrographic technique is also finding application in solving problems concerning coal beneficiation.

Coal macerals can be defined as the microscopically recognizable organic constituents having no definite crystal structure and chemical composition. These macerals are generally classified into three major maceral groups and each group represents the maceral having uniformly similar properties in a coal of specific