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PREFACE

A systematic investigation has been carried out on seven kaolin samples collected from the major deposits in India, i.e., Kasargod and Trivandrum (Kerala), Koraput (Orissa), Kutch (Gujarat), Bankura (West Bengal) and Pali (Rajasthan). The total work is presented in 7 chapters. Chapter 1 deals with the general introduction on kaolin with respect to its formation, mineralogical and structural aspects, unique properties and industrial uses. This chapter also describes the iron minerals associated with kaolin and their effect on the optical properties. The national / international status on kaolin research is also discussed.

Chapter 2 explains the methodology adopted for characterization of clays and impurity minerals. The techniques involved are wet chemical analysis, ICP-AES, UV-Vis spectrophotometry and flame photometry for chemical assay, XRD and thermal analysis (DTA/TGA) for mineralogy, particle size distribution analysis, brightness and colour measurements, EPR, Mossbauer, FTIR and UV-Visible spectroscopy and electron microscopy (SEM, HR TEM - EDS and EPMA). Procedures for the methods adopted for concentration / removal of impurity minerals are also given.

Results on the characterization of the run-of-mine (ROM) and size classified kaolins are presented in Chapter 3. This chapter also gives details on the speciation of iron minerals and suggests the methods for value addition of kaolin. All clays under study are highly kaolinitic and the quantity and type of ancillary minerals vary from clay to clay. Quartz is the common impurity and micaceous, ferruginous and carbonaceous minerals also exist either singly or in combination. The three kaolin samples from Kerala are kaolinitic with impurities of quartz, rutile, anatase and iron oxides / hydroxides. Pyrite is the major iron impurity in Koraput clay whereas mica dominates in Pali and Bankura samples. The Kutch kaolin is associated with iron stained titania. Size classification increases the percentage of fine fraction. The optical properties of the clays also improve during size classification due to the removal of the coarse colored minerals. DCB treatment has given a picture of the total soluble/free iron in the samples. Kaolins from Kasargod, Trivandrum, Koraput and Bankura respond well to the DCB treatment. Pali and Kutch samples show very poor response.
Chapter 4 gives an account of the separation of impurity minerals by hydrocycloning, panning, alkali treatment and magnetic (hand magnet) techniques and their chemical and mineralogical characterization. The iron content in the impurity is high, but XRD analysis indicated low crystallinity. It is reasonable to think that the same minerals may be present in the clay as fine particles. Hematite and goethite are found to be major ancillary minerals present in Kasargod and Trivandrum clays with some ilmenite in one sample. Kutch clay contains mostly anatase and hematite, whereas Koraput sample contains pyrite and goethite. Goethite and mica are found in Bankura and Pali samples with some hematite in the former and calcite in the latter. It is observed that size classification removes most of the quartz but does not significantly remove the coloring impurities except in a few cases. Uniform distribution of these impurities in all size fractions is thus indicated.

Chapter 5 is on the spectroscopic (EPR, Mossbauer, Infra red and UV-Visible) and microscopic (Optical, SEM, HR TEM-EDS and EPMA) studies on selected samples. The spectroscopic and microscopic data obtained clearly substantiate the findings detailed in Chapters 3 and 4. The EPR spectral studies of selected samples were carried out at room temperature to characterize the minor components in clays that contain unpaired electrons and also to assess the effectiveness of chemical bleaching. Since the iron content in the clay samples was too low to be measured by the instrument, the impurity minerals concentrated by panning were subjected to the Mossbauer spectral studies. The characteristic isomer shift (\( \delta \)), quadruple splitting (\( \Delta E \)) and K\( \Omega \)e values obtained from the spectra gave information on the type of iron impurity. FT IR studies explain the ordering in kaolinite, its crystallinity, and the presence of impurity minerals. UV-Visible spectral studies on impurity minerals concentrated by panning was carried out to identify the iron species present based on their electronic spectra i.e., (i) Fe\(^{3+}\) Ligand Field Transitions (ii) Ligand to Metal Charge Transitions and (iii) transitions resulting from the simultaneous excitation of magnetically coupled Fe\(^{3+}\) cations which occupy adjacent sites.

Electron Probe Micro Analysis (EPMA) of ROM and impurity separated by hydrocycloning gave the distribution pattern of the elements indicating the mineralogy. ROM and size classified products (SCP1 and 2) of the clays were examined under SEM
to understand the size and shape of the particles. Due to the uniqueness of the impurity 
minerals in Kutch and Koraput clays, HR TEM –EDS of selected samples from these 
clays were taken to get a detailed particle wise microanalysis data.

In Chapter 6, an attempt has been made to correlate the Fe-Ti content in the clays 
with their optical properties. It has been observed that the total iron content (analytical 
iron) cannot be directly related to the optical properties of the clay. Iron can exist in two 
forms, “structural” and “free” which has been distinguished by their response to the DCB 
treatment. Small amount of iron in kaolinite structure does not affect the brightness 
because the Fe atoms are too far apart to allow any electronic transition. However, the 
same amount of Fe if present in the small quantities of ancillary minerals imparts color 
and affects the brightness of kaolin. Hence, the optical properties of kaolin are not 
directly related to the “analytical” iron content, but are dependent on the species of iron 
present in the clay.

The investigation on Koraput kaolin has been discussed in Chapter 7. During the 
size classification studies, it was observed that the conventional method could not be 
adopted for this clay due to the high acidity. The clay water slurry was yellow in color 
and resulted in precipitation during dilution. Subsequent filtration and drying resulted in a 
product with yellowish brown color. Detailed study was conducted to solve this problem 
and a modified method has been suggested to get product clay of acceptable brightness.

Conclusions drawn out of the detailed investigations of the kaolins are given at 
the end. This includes results of the characterization of the ROM clay, beneficiated 
products and the impurity minerals, correlation of the Fe and Ti minerals with the optical 
properties, suggestions on the possible value addition by using advanced processing 
techniques and comparison of the product samples with Indian and international 
specifications for different applications. All the results have been published in journals 
and / or presented during national and international conferences.