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RESEARCH ARTICLE

MINEROLOGICAL STUDY OF CLAY SAMPLES AND CLAY MINES AT DIFFERENT DEPTHS IN CUDDALORE DISTRICT, TAMILNADU, INDIA

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ABSTRACT

Clay minerals play an important role in the gravitational stability of man-made rock piles by affecting geotechnical and hydrological characteristics of the material. FT-IR technique is used to distinguish between different types of minerals and to derive information concerning their structure, composition and structural changes upon chemical modification. The selections of the sample technique used depend on the purpose of the study and on the physical state of the sample. KBr pressed disk technique was found to be very useful for a routine characterization of both di and trioctahedral clay minerals. We have studied the mineralogical characteristics of clay deposits from Keeliruppu, Panruti, Cuddalore District, Tamilnadu, India. To determine their composition and possible use in local industry. The studied deposits are chemically homogenous, except for the samples richer in kaolinite and sand fraction. The clay samples were subjected to FT-IR analysis in the region of 4000 - 400 cm^{-1}, which can be used to characterize the different minerals. The mineralogical composition of the clays has demonstrated that, taken as a whole, they possess characteristic satisfactory for brick production.

INTRODUCTION

Clay minerals share a basic set of structure and chemical characteristic (e.g. they are largely alumino silicates with layer structures) and yet each clay mineral has its own unique set of properties that determine how it will interact with other chemical species. The variation, in both chemistry and structure, among the clays leads to their applications of clays are in the manufacture of paper, paint, plastics and rupper. One of their more recent and most economically important applications is in the perlitter industry where their adsorptive and deodorizing properties are used. Those who exist with scarce resources frequently collect clay from local deposits and ingest them as a source of dietary minerals. It is different for a day to go without using a product incorporating clay minerals, as we all use ceramics such as dinner ware and sanitary ware Patricia, et al. (2001).

Clay occurs widely in many ports of Cuddalore District Tamil Nadu. Beside their geological interest, they are of importance for local industry. They have been used to produce rather poor quality bricks, tiles and pottery by primitive methods for several years. Scattered clay pits and brick kilns along the riverbed sides document the uncontrolled and low-technology exploitation of the Cuddalore District, Tamil Nadu clay occurrences.

The above-mentioned brick and tile industries (kilns) cannot meet the ever –increasing market demand for the construction materials needed. Traditional methods of production, which do not take account of the chemical and mineralogical characteristics, are still practiced. In the traditional method of brick production, raw clay material is mixed with water and covered for about a week. The paste is placed in a wooden mould and the bricks are spread and covered with cut grass until they are dry. However, during the rainy season, Plastic sheets are used to cover the bricks. The bricks are fired infield kilns, which consist of a large pile of unfired bricks with tunnels in the bottom of the pile. The pile is cemented with clay and contains 10,000-15,000 bricks. A wood fire is built in the tunnel and kept burning for 4-6 days and the tunnels are then closed with unfired bricks and also cemented with clay. The hot exhaust from the wood fire flows through the pile, and heats the center of the pile enough to fire the bricks in the core of the pile. The pile is then allowed to cool and dismantled George et al. (2002).

A study of some clay samples from Keeliruppu deposits in Cuddalore District, Tamil Nadu indicates that they are medium quality kaolinite clay. There is sample demand for quality bricks and other clay products, and, thus, the present study evaluates the mineralogical and chemical characteristics of the raw material used, not only in individual brick and tile works, but also by the traditional potters. This will help to give a better understanding of the clay materials.

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METHODS AND METHODS

In these studies we analyzed (S1, S2, S3, S4, S5, S6 and S7) 7 clay samples taken from deposit that supply construction industry in Keeliruppu clay mines, Cuddalore District, Tamil Nadu, and India. Well mixed large samples, which were reduced to about 250 g each by coning and quartering, were taken from clay mines each sample has 5m distance apart, were crushed in a agate mortar and a fraction of the clay samples were used for FT-IR analysis of structural characterization of the <2µmfraction of clay. Samples were dried at 60°C, and divided for mineralogical analysis. Mineralogical analysis was performed at centralized instrumentation servicing laboratory (CISL), Department of Physics Annamalai University, Tamil Nadu, India.

RESULTS

In the infrared study their respective infrared spectra were presented in the Fig 1.The IR spectra show the peaks of kaolinite, quartz, montmorillonite and hematite. In the seven (different depths) samples namely S1, S2, S3, S4, S5, S6 and S7 the presence of very strong band at 3695 cm^{-1} along with the weak band at around 1640 cm^{-1} are due to adsorbed water.

Table 1. The Infrared absorption frequencies (cm^{-1}) for Keeliruppu clay samples at different depths

S1	S2	S3	S4	S5	S6	S7	Tentative Assignment	Minerals Name
Freq.	Freq.	Freq.	Freq.	Freq.	Freq.	Freq.		
3695	3696	3696	3696	3696	3697	3696	OH- stretching of inner hydroxyl bonding	kaolinite
3667	3668	3669	3667	3668	3667	3667	Degenerate internal Surface free OH anti symmetric stretching mode stretch (Al_2O-H)	kaolinite
3650	3653	3650	3654	3655	3654	3654		
3620	3620	3620	3620	-	3620	3620	OH stretching of inner hydroxyl bonding	kaolinite
3432	3436	-	-	-	-	-	H- O-H vibration of absorbed water	Montmorillonite
2904	2903	2904	2905	2904	2904	2902	C-H –Stretching	Organic mater in kaolinite
2812	2813	-	2815	-	-	2813	C-H –Stretching	Organic mater in kaolinite
-	1635	1636	1636	1636	1637	1637	H-O-H Bending vibration of absorbed water molecule	kaolinite
1625	-	-	-	-	-	-	H-O-H deformation	kaolinite
-	1113	1112	1113	1112	1112	1114	(Al-O-(OH))6	Montmorillonite
1100	-	-	-	-	-	-	Si-O stretch hydrogen bonded to H_2O	kaolinite
1033	1032	1032	1032	1031	1031	1032	Si-O of stretching	kaolinite
1009	1007	1007	1006	1006	1007	1007	Si-o-Si-symmetric stretching	kaolinite
913	913	913	913	913	913	913	Al_2 OH bending	kaolinite
796	794	793	792	794	793	794	-	kaolinite
779	-	-	-	-	-	-	Si-O of Quartz	Quartz
-	-	753	753	755	754	754	-	kaolinite
694	695	696	697	695	695	696	Si-O of Quartz	Quartz
539	538	538	538	538	538	537	Fe-O (Fe_2O_3)	Hematite
470	469	468	468	469	468	469	Si-Oasymmetric bending vibration	Quartz
432	431	431	431	430	430	431	Si-O of mixed vibration	kaolinite

In addition a well marked absorption around 3667, 3650 and 3620 cm^{-1} were found. It is well established that the infrared absorption bands in the 3800-3600 cm^{-1} region in the spectra of clay minerals are due to the stretching vibrations of free hydroxyl groups present in them. All the samples give very strong broad band in the 1000cm^{-1} region which is characteristics of silicate minerals. In the case of all the samples from Keeliruppu clay mines, this band is found to be centered around 1030 cm^{-1} with very strong intensity indicating red clay origin of the Kaolinite clay. The relatively broad band in all spectra (Fig.1) at 1100 cm^{-1} is assigned to the inner Si-O stretching hydrogen bonding to H_2O, and this broading is an indication of hydrogen bonding. The weak bond at 913 cm^{-1} which appears in all spectra of Fig 1. The deformation modes of inner surface of Al_2O-H deformation modes.

Relative distribution of minerals

The relative distribution of major mineral Kaolinite (K) and Quartz (Q) can be found out using extinction co-efficient K by the relation $K=DA/M$

Apparently a mineral with a high degree of crytallinity needs more energy for its transformation to a new structure than a mineral of poor crystallinity. Similarly from the table 2, the lowest and highest extinction co-efficient values are known. They are illustrated graphically and moreover, this data was nearly same as the previous data, so it is not necessary to discuss about the quartz (694 cm^{-1}) so that the extinction co-efficient for kaolinite and quartz of seven different depth samples (S1 to S7) are discussed in table 2 it can be observed from the frequencies 1033 cm^{-1} and 694 cm^{-1}. The 20th feet sample having maximum absorbance of 28.052, from the Figure (2) the lowest amount of minerals kaolinite and quartz obtained at S2 and S4. The invariable presence of quartz and kaolinite. In all the samples indicates that there are ubiquitous minerals in clays.

Table 2. Extinction co-efficient of Kaolinite 1030 cm^{-1} and Quartz694 cm^{-1}

Depth in feet	Kaolinite 1033 cm^{-1}		Quartz 694 cm^{-1}	
	D=log(I_0/I)	K=DA/M	D=log (I_0/I)	K=DA/M
5	0.1906	8.429	0.09156	4.0581
10	0.6154	26.336	0.1658	7.0958
15	0.3273	14.475	0.0704	3.114
20	0.5920	28.052	0.1541	7.3032
25	0.3467	16.43	0.1110	5.2609
30	0.3537	15.137	0.08566	3.6660
35	0.5383	24.625	0.1429	6.5394

Table 3. Statistical data for Kaolinite1030 cm^{-1} and Quartz 694 cm^{-1}

Statistics	Kaolinite 1033cm^{-1}	Quartz 694 cm^{-1}
Range	8.43-28.05	3.11-7.30
Arithmetic Mean	19.069	5.291
Standard Deviation	7.315	1.720
Skewness	-0.060	-0.023
Kurtosis	-1.522	-2.144
Frequency Distribution	Normal	Non-Normal

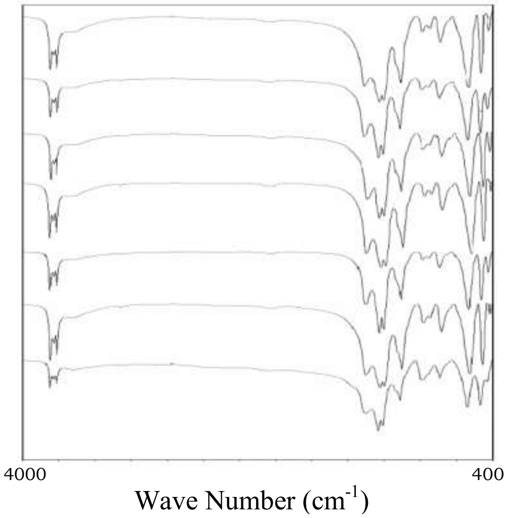

Fig. 1. Infrared absorption spectra of Keeliruppu clay (KLP) samples at different depths

Statistical method (or) analysis

An attempt is made to use the statistical method to find out the distribution pattern of the minerals. The statistical values corresponding to minerals (Kaolinite 1033 cm^{-1} and Quartz 694 cm$^{-1)}$ and its extinction co-efficient are measured for clay and non-clay samples are presented in Table 2. The respective mean value, standard deviation, range, skewness, kurtosis co-efficient and the frequency distribution are listed in Table 3.

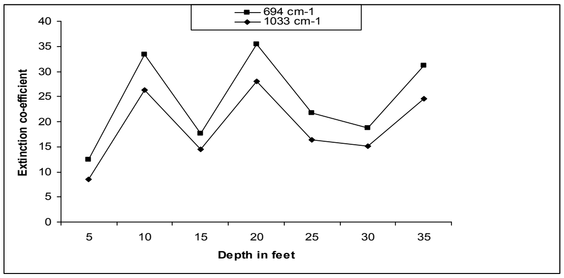

Fig. 2.Depths versus extinction coefficient for Kaolinite (1033 cm^{-1}) and quartz (694 cm^{-1}) in clay samples

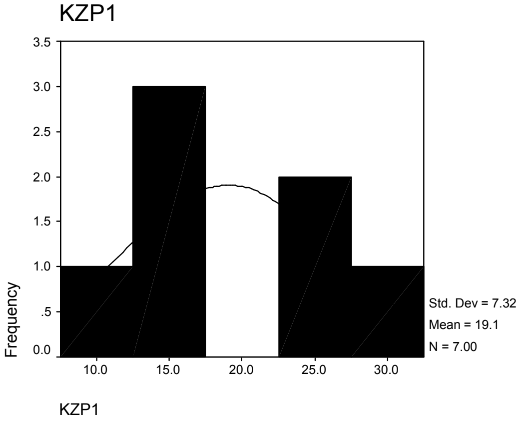

Fig.3 (a). Frequency distribution of extinction co-efficient of Kaolinite (1033 cm^{-1})

The frequency distribution of the mineral (Kaolinite) detected. It can be observed from the Table 3 and Fig 3 for Kaolinite (1033 cm-1) that the negative value of skewness of the site (KLP) clay is 0.060. Fig. 3(a) shows that its distributions are symmetric for the sample. It can be obtained from the Fig. 3(b) for (Quartz 694cm-1) reveals a high level abundance of Quartz mineral in samples (S2 and S4) and the lowest amounts are produced by the samples (S3 and S5). It can be obtained from the Table 3 for (Quartz 694 cm^{-1}) that the negative value of skewness 0.023. Fig. 3(b) shows that its distributions are asymmetric with left tail longer than the right. Negative and lower value of skewness obtained. This is due to the uneven spatial distribution of quartz (694 cm^{-1}) in the clay of KLP clay mines. Both the statistical and graphical representation gives useful information of distribution pattern of the minerals.

Brick manufacture is associated with a number of environmental implicated, some of which are beneficial, and other which are potentially detrimental. Traditionally, bricks have been and are produced in fraction, which are sited adjacent to the source of the clay. The life of the production site may extend beyond in life of an associated

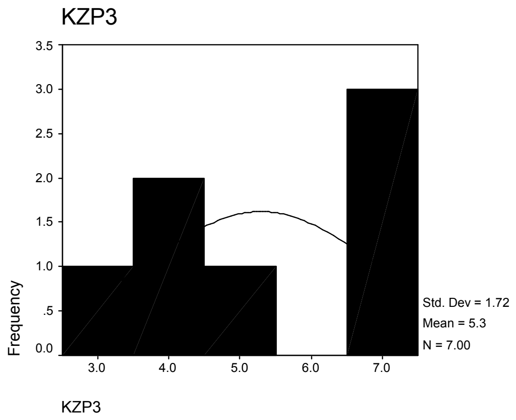

Fig.3(b). Frequency distribution of extinction co-efficient of Quartz (694 cm^{-1})

quarry, or beyond individual phases of quarrying yielding large excavations in the vicinity of the plant.

DISCUSSION

The valuables information about the samples of crystallinity and regularity of structure of clay minerals Russell et al. (1987). In addition a well marked absorption around 3667, 3650 and 3620 cm^{-1} were found. It is well established that the infrared absorption bands in the 3800-3600 cm^{-1} region in the spectra of clay minerals are due to the stretching vibrations of free hydroxyl groups present in them. Kaolinite which is the major constituent of clay Keeliruppu clay samples gives sharp absorption bands in the 3700-3600 cm^{-1} region. A comparison of these spectra with the spectra of Ramasamy et al. (2000) indicates that all these correspond to well order Kaolinite structure. It has been pointed out that the bands at 3695 cm^{-1} and 3620 cm^{-1} are attributed to outer and inner hydroxyl groups and that the 3695cm^{-1} has a maximum intensity in well ordered Kaolinite structure while 3620 cm^{-1} does not change in intensity Ramasamy et al. (1992).

The weak bands around 2900 cm^{-1} and 2810 cm^{-1} occur in C-H stretching region Colthup et al. (1990) the very weak intensities of these bands could be an indication of traces of organic matter in Kaolinite from the Keeliruppu clay mines. The band at 1618 cm^{-1} is assigned to H_2O deformation mode of the adsorbed water. The fine structure lines around the band at 1618 cm^{-1} which is extended from about 1800 to1300 cm^{-1} is due to rotational, transitions accompanied the vibrational transitions at 1616 cm^{-1}. This assignment is in very good agreement with the previous study Wilson et al. (1994). Another indication of the presence of ordered Kaolinite is the appearance of the two weak bands at 796 and 754 cm^{-1} Cole et al. (1979). It should be mentioned, that the weak bands at 796,754 and 694 cm^{-1} may also be considered as lattice vibrations of Quartz Wilson et al. (1994). This means that there is a possibility that Quartz may be present in Kaolinite, however, the weak intensities of these bands may indicate that it occurs in very small amount. The weak bands at 796 and 754 cm^{-1} are superimposed in Kaolinite and Quartz. All these samples show very strong absorption band around 535 cm^{-1} they are due to hematite (Fe_2O_3). This band shows that the crystalline hematite are present in all samples Ghosh et al. (1978).The bands at 470 cm^{-1} and 430 cm^{-1} have been assigned to Si-O of asymmetric bending vibration and Si-O of mixed vibration respectively.

CONCLUSION

The presence of kaolinite and quartz present in almost all the samples indicate that there are ubiquitous minerals in clay samples. The presence of FTIR absorption peaks 1030, 913 and 694 cm^{-1}may give useful information on nature of the minerals with regard to stability. The ant symmetric stretching of Si-O-Si group obtained at 1030 cm^{-1} and the internal surface of Al_2O-H group obtained at 913 cm^{-1}. The symmetrical bending vibration of Si-O group obtained at 694 cm^{-1} is more useful to find whether it is a crystalline or amorphous. The 913, 694cm^{-1} peaks are exhibited by the spectra for the all clay samples. The kaolinite minerals in these samples are well crystalline form. The distribution of the clay and non-clay minerals (Kaolinite and Quartz) found out using the extinction co-efficient. Overall, the clay studied here exhibit a wide range of mineralogical compositions. The clay raw materials fundamentally consist of kaolinite and quartz, with rare montmorillonite and minor iron oxide. An important role seems to be played by the minor mineralogical components, which influence the firing color. However, due to the generally high quartz contents they may possess a refractory behavior. These clays have chemical mineralogical compositions that indicate their usefulness for brick, ceramics and earthenware production. Further systematic applied testing of the clays has yet to be carried out to determine their physical, mechanical, and technological properties.

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