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# X Rays, IR, DTA, TGA and TG studies of Rajmahal Hills Bentonites of Jharkhand in India.

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## ABSTRACT

Researchers in past have studied the characteristics of Bentonite from various places in India. Bentonite of Rajmahal Hills in Jharkhand, however was considered as a low quality Bentonite since many years. The authors of the paper have undertaken extensive study on various bentonites from Rajmahal hills and undertaken analysis of these samples using X-rays, IR, DTA, TGA and TG in order to evaluate the quality of this bentonite. The absorption band of IR spectra when correlated with literature confirms the presence of Montmorillonite as major clay mineral in the Bentonite minerals of Rajmahal hills. The d spacing values of X ray powder data of the same too substantiates the presence of Montmorillonite clay mineral in all the samples along with Kaolinites and Smactites in small proportions. DTA and TGA studies show high temperature endothermic peak between 550 °C and 750 °C resulting from the lattice water indicating the presence of Montmorillonite. Hence it has been found for the first time that these bentonites are high quality bentonite and can been utilized for commercial use.
**Keywords:** Bentonite, Rajmahal bentonite, Analysis, X ray, IR, DTA, TGA, TG

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## INTRODUCTION

India marked 1938 as the year of the studies of Bentonite, first from Rajasthan [1] followed by the work of Bhola [2], Raja Rao [3], Chaliha [4], Bishui [5] and Guha [6], declaring the Bentonite of Rajmahal Hills as low quality Bentonite, which really stopped further work on this. It was traced later that these Bentonites had been collected from nearby sites of Tinpahar, Bakudih, Taljhari, Pirpainti, all Railway Stations on Sahibganj loop line from Kiul to Howrah and vast deposits of Bentonite in hills and woods were left untouched. In continuity of the investigations of large number of Bentonites were collected from different places of Rajmahal Hills [7-12] for the first time. Studies on X-rays, IR, DTA, TGA and TG data are reported in order of evaluation of the quality for their suitability for commercial and social usage.

X-rays technique was used for identification of the Montmorillonite group of minerals [13]. Early to this, Keppler and Aurich [14] studied X-rays of Montmorillonite and Kaolinite clay. X-rays and infra-red studies of some Bentonite samples of Rajmahal Hills have been done [7]. Bagchi studied thermal and optical properties of minerals present in Hydrogillite Clay from Indian soil Kaolinites and Bentonites [15].

Some work on X-rays and thermal studies of some Indian Montmorillonite have appeared in literature [16] where no mention has been made about the Bentonite minerals of Rajmahal Hills in Santhal Praganas of Jharkhand, India. DTA technique was used for the study of minerals like Montmorillonite, Kaolinite, Hydrogillite, Limonite etc [17]. DTA of Montmorillonite clays was also studied by Orcel and Coillere [18]. In addition to all the properties with theoretical formula from chemical composition [7-12], X-rays, IR and thermal properties of some of the important Rajmahal Bentonite samples not studied earlier are reported here.

## EXPERIMENTAL

The Bentonite samples giving blue colour to the benzidine solution in alcohol were collected from different places in Rajmahal hills earlier coded as SRHB (Santhal Pargannas Rajmahal Hills Bentonite) in literature [7-12] have been reported with the name of the places in Table 1.

**Table - 1: Details of Bentonite samples**

| Sample Number | Place |
|---|---|
| SRHB -1 | Bakudih |
| SRHB -3 | Mandali Mirjachaunki |
| SRHB -4 | Baldhatri Mirjachaunki |
| SRHB -5 | Bakudih |
| SRHB -6 | Bakudih |
| SRHB -7 | Motijharna Bangla Maharajpur |
| SRHB -8 | Simaljuril (Bangla Taljhari) |
| SRHB -9 | Bakudih |
| SRHB -10 | Bhut bangla East of Mirjachaunki |
| SRHB -11 | Madhyo bari pahar west to banjhi |

| | |
|---|---|
| SRHB -12 | Kusma phatak (Kotal pokhar) |
| SRHB -13 | Madhyo bari pahar west to banjhi |
| SRHB -14 | Balbhadri |
| SRHB -15 | Garara pahar west to Mirjachaunki |
| SRHB -16 | Ranidih west to Mirjachaunki |
| SRHB -19 | Brindavan-1 |
| SRHB -20 | Brindavan-2 |
| SRHB -22 | Sihli mines 2 |

**Table - 2: IR Absorption Frequencies of Bentonite minerals of Rajmahal Hills in $cm^{-1}$**

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample Number/ Place | | | | | | | | | | | | |
| SRHB -1 | 685 | 745 | - | 850 | 965 | 1035 | 1105 | - | 1570 | - | 3500 | - |
| Bakudih | 915+ | 1030+ | 1640+ | 3400+ | 3675+ | | | | | | | |
| SRHB -3 | - | - | - | - | 900 | 1030 | - | 1380 | 1570 | 2360 | 3500 | - |
| Mandali Mirjachaunki | 915+ | 1030+ | 1640+ | 3440+ | - | | | | | | | |
| SRHB -4 | 680 | 775 | - | 810 | 950 | - | - | - | 1580 | 2385 | - | 3580 |
| Baldhatri Mirjachaunki | | | | | | | | | | | | |
| SRHB -5 | - | 735 | 775 | 830 | - | - | - | 1585 | - | - | 3600 | |
| Bakudih | | | | | | | | | | | | |
| SRHB -6 | - | 740 | 780 | - | 970 | - | - | - | 1560 | 2360 | 3460 | - |
| Bakudih | | | | | | | | | | | | |
| SRHB -7 | 650 | 740 | 775 | 850 | 950 | - | - | - | 1560 | 2360 | 3540 | - |
| Motijharna Bangla Maharajpur | | | | | | | | | | | | |
| SRHB -8 | - | 665 | 730 | 780 | 835 | 950 | 1575 | 1640 | 1800 | 2370 | 3660 | 3680 |
| Simaljuril (Bangla Taljhari) | 750+ | | 915+ | 1030+ | 1640+ | - | | 3680+ | | | | |
| SRHB -9 | - | 670 | 740 | - | 840 | 970 | 1580 | - | 1780 | 2300 | - | - |
| Bakudih | | | | | | | | | | | | |
| SRHB -10 | 500 | 650 | 730 | 775 | 830 | 960 | 1520 | - | - | 2360 | 3740 | - |
| Bhut bangla East of Mirjachaunki | | | | | | | | | | | | |
| SRHB -11 | - | - | 745 | - | 850 | 970 | 1560 | - | - | - | 3600 | - |
| Madhyo bari pahar west to banjhi | | | | | | | | | | | | |
| SRHB -12 | - | - | 755 | 780 | 840 | 970 | 1560 | - | 1800 | 2370 | 3530 | 3650 |
| Kusma phatak (Kotal pokhar) | 750+ | 790+ | 915+ | 1000+ | 1050+ | 1650+ | 3460+ | 3680+ | | | | |
| SRHB -13 | - | 640 | 690 | - | 865 | 970 | 1365 | 1730 | - | 2380 | - | - |
| Madhyo bari pahar west to banjhi | - | 765+ | 915+ | - | 1040+ | 1650+ | 3440+ | - | | | | |
| SRHB -14 | - | - | - | - | 1580 | 2000 | 2370 | - | 3560 | - | | |
| Balbhadri | | | | | | | | | | | | |
| SRHB -15 | - | - | - | - | 1570 | - | 2370 | - | 3560 | - | | |
| Garara pahar west to Mirjachaunki | | | | | | | | | | | | |
| SRHB -16 | - | 765 | 840 | 950 | 1580 | - | - | 2600 | 3580 | - | | |
| Ranidih west to Mirjachaunki | | | | | | | | | | | | |
| SRHB -19 | - | - | - | - | 1570 | - | 2380 | - | - | 3680 | | |
| Brindavan-1 | | | | | | | | | | | | |
| SRHB -20 | - | 765 | 825 | 940 | 1570 | - | 2375 | - | - | - | | |
| Brindavan-2 | | | | | | | | | | | | |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SRHB -22 | 690 | 750 | - | - | 1580 | - | 2380 | 2680 | 3480 | 3640 | | |
| Sihli mines 2 | 750+ | 915+ | 1030+ | 1650+ | 3460+ | 3640+ | | | | | | |
| | | | | | | | | | | | | |
| + Ambi S., Jha N.K., Prasad M.M., and Mishra Bivekanand, J. Ind. Chem. Soc., 1978, 55, 1077-1079. | | | | | | | | | | | | |

**Table - 3: X-ray powder data of Bentonite minerals of Rajmahal Hills in d (Å)**

| Name of place | Code number | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Bakudih | SRHB -1 | 4.3391 | 2.6714 | 2.4913 | 15.2910 | | | | |
| Baldhatri Mirjachaunki | SRHB -4 | 4.3921 | 2.5917 | 2.4930 | 15.2101 | | | | |
| Bakudih | SRHB -5 | 4.4101 | 2.5917 | 2.4123 | 15.2915 | | | | |
| Motijharna Bangla Maharajpur | SRHB -7 | 7.2281 | 4.4992 | 4.3192 | 3.5989 | 2.4969 | 2.2919 | | |
| Bakudih | SRHB -9 | 4.4783 | 3.6020 | 2.4310 | 15.8310 | | | | |
| Madhyo bari pahar west to banjhi | SRHB -11 | 6.6781 | 4.4783 | 3.6021 | 2.4310 | 15.8310 | | | |
| Brindavan-2 | SRHB -20 | 4.3260 | 2.5498 | 2.5012 | 15.3101 | | | | |
| Mandali Mirjachaunki | SRHB -3* | 4.3533 | 2.8400 | 2.4947 | 15.5044 | | | | |
| Simaljuril (Bangla Taljhari) | SRHB -8* | 4.5521 | 4.3323 | 3.6627 | 2.5996 | 2.3324 | | | |
| Kusma phatak (Kotal pokhar) | SRHB -12* | 6.5588 | 4.2300 | 4.0042 | 3.4662 | 3.2434 | 2.4947 | 2.2813 | |
| Madhyo bari pahar west to banjhi | SRHB -13* | 4.4838 | 3.5900 | 2.5287 | 15.7810 | | | | |
| Balbhadri | SRHB -14* | 4.5064 | 4.2909 | 3.7547 | 3.1318 | 2.2813 | 2.7467 | 15.5044 | |
| Sihli | SRHB -22* | 5.0676 | 3.5900 | 3.0481 | | | | 15.2373 | |
| Bihar** | | 7.23(K) | 4.48(M) | 3.34(I) | 2.57(M) | 15.77(M) | | | |
| Rajula** | | 10.1(I) | 4.48(M) | - | 2.58(M) | 15.40(M) | | | |
| Akli** | | 7.17(K) | 4.48(M) | - | 2.57(M) | 15.50(M) | | | |
| Hathisingh ki dhani** | | 7.18(K) | 4.47(M) | - | 2.57(M) | 15.41(M) | | | |
| Jaipur** | | 4.49(M) | 3.34(I) | - | 2.59(M) | 2.57(I) | 11.40(M+I) | | |
| Karauli** | | 5.03(I) | 4.48(M) | - | 2.54(M) | - | 11.80(M+I) | | |
| Montmorillonite calculated | | 4.5000 | 2.6000 | 2.2500 | 1.7060 | 1.5030 | 1.3011 | 1.2520 | |
| Kaolinite calculated | | 7.1500 | 4.4000 | 4.3320 | 4.1720 | 3.7360 | 3.5780 | 3.1480 | 3.0980 |
| | | 2.7480 | 2.5660 | 2.4830 | 2.3350 | 2.8800 | | | |
| * Ambi S., Jha N.K., Prasad M.M., and Mishra Bivekanand, J. Ind. Chem. Soc., 1978, 55, 1077-1079. | | | | | | | | | |
| ** Guha S.K. and Sen Sudhir, Trans. Ind. Ceramic Soc., 1973, 32 (5), 97-104. | | | | | | | | | |
| *** Ambi S, The study of Betonite Minerals from Rajmahal, Bihar, IIT Delhi (1977) | | | | | | | | | |

**Table - 4: Differential Thermal Properties of Bentonite minerals of Rajmahal Hills**

| Code number | Endothermic (size) | Exothermic (size) | |
|---|---|---|---|
| SRHB -1 | 189(small) | 950(medium) | |
| Bakudih | 567(large) | | |
| SRHB -3 | 218(large) | | |
| Mandali Mirjachaunki | 914.5(small) | | |
| SRHB -4 | 170(large) | 912(small broad) | |
| Baldhatri Mirjachaunki | 503(small | | |

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| | | | |
|---|---|---|---|
| | broad) | | |
| SRHB -5 | 212(medium) | | |
| Bakudih | | | |
| SRHB -6 | 207(large) | | |
| Bakudih | 676(large) | | |
| SRHB -7 | 140(medium) | 918(small) | |
| Motijharna Bangla Maharajpur | 524(large sharp) | | |
| SRHB -9 | 186(medium) | 927(small broad) | |
| Bakudih | 556(medium) | | |
| SRHB -19 | 148(small) | 808(small) | |
| Brindavan-1 | 582(large) | | |
| Bihar* | 145(large) | 980(sharp medium) | |
| | 580(medium) | | |
| | 712(small) | | |
| Rajula* | 160(large) | | |
| | 550(small) | | |
| | 620(small) | | |
| | 855(small) | | |
| Akli* | 160(large) | 920(small broad) | |
| | 550(medium) | | |
| Hathisingh ki dhani* | 155(large) | 930(small broad) | |
| | 560(medium) | | |
| Jaipur* | 120(medium) | 980(small) | |
| | 685(small) | | |
| | 880(small) | | |
| Karauli* | 120(medium) | 980(small) | |
| | 680(medium) | | |
| | 890(small) | | |
| | | | |
| ** Guha S.K. and Sen Sudhir, Trans. Ind. Ceramic Soc., 1973, 32 (5), 97-104. | | | |

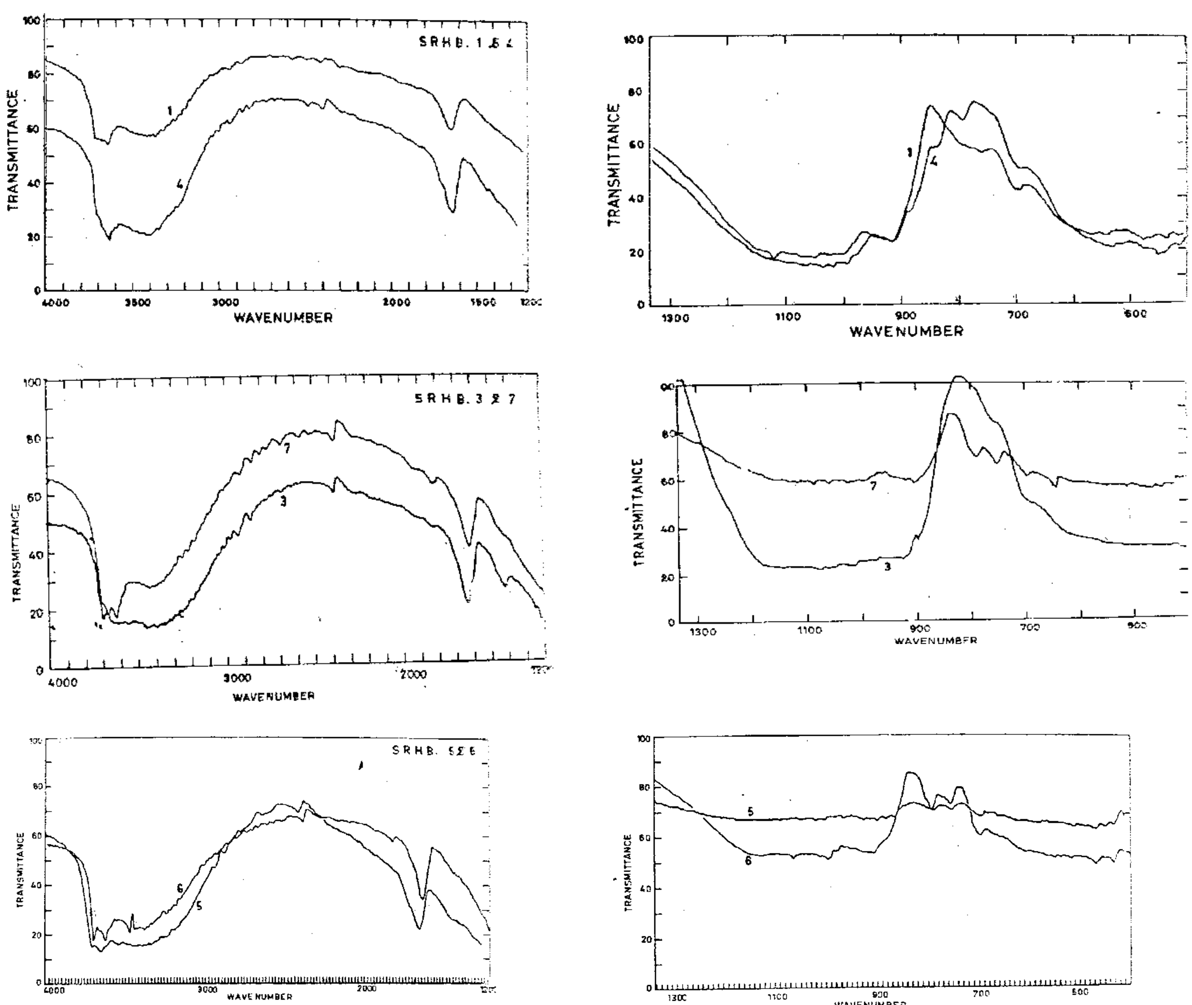
**Table - 5: DTA data of Bentonite minerals of Rajmahal Hills**

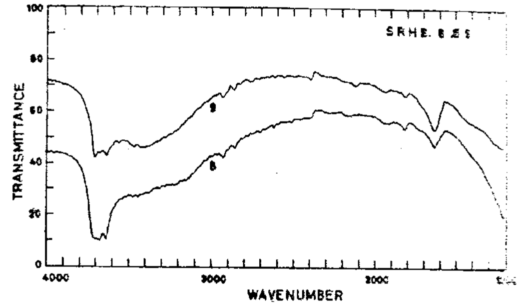
| Name of place | Code number | Weight of sample in mg | Loss of sample in mg | Percentage loss of sample in mg |
|---|---|---|---|---|
| Bakudih | SRHB -1 | 600 | 113 | 18.83 |
| Mandali Mirjachaunki | SRHB -3 | 600 | 146 | 24.33 |
| Baldhatri Mirjachaunki | SRHB -4 | 600 | 118 | 19.60 |
| Bakudih | SRHB -6 | 600 | 144 | 20.57 |
| Motijharna Bangla Maharajpur | SRHB -7 | 600 | 143 | 20.42 |
| Bakudih | SRHB -9 | 600 | 126 | 18.00 |
| Brindavan-1 | SRHB -19 | 600 | 80 | 13.33 |

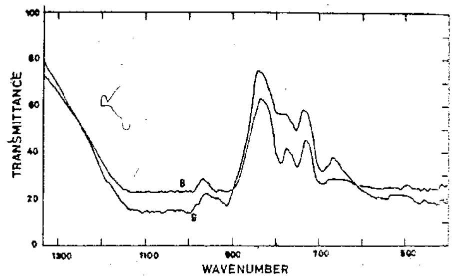
Hilger Watts IR Spectrophotometer in the Chemistry Department of Indian Institute of Technology, New Delhi was used in the region 4000 -700 cm$^{-1}$ for the samples reported here. The IR observed data have been reported in Table 2 along with literature values of some Bentonites for comparative study [6]. The corresponding IR curves have been given in Figure 1 traced transmittance vs. wave number. Phillips Diffractometer in the X-ray laboratory of Textile Department of Indian Institute of Technology, New Delhi and X-ray unit XRD of General Electrical USA in Indian Institute of Petroleum, Dehradoon were used for X-ray powder data are tabulated in Table 3 along with literature values and calculated values of Montmorillonite and Kaolinite for comparison.

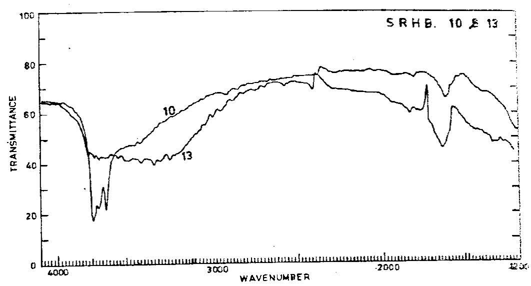
DTA, TGA and TG instruments present in the Chemistry Department of Indian Institute of Technology, New Delhi were also used for the present samples and these data obtained are recorded in Table 4 and Table 5. The corresponding curves are shown in Figure 2.

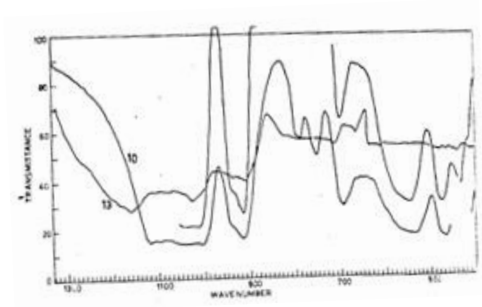
**Figure 1. IR Absorption curves of Bentonite Minerals of Rajmahal Hills**

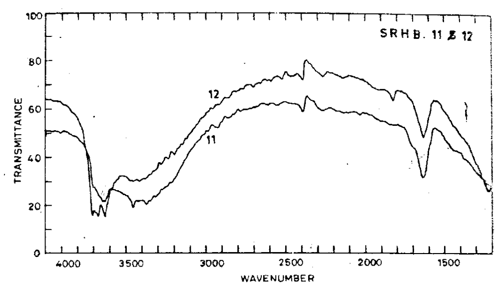



SRHB. 8 & 9
TRANSMITTANCE
WAVENUMBER


TRANSMITTANCE
WAVENUMBER


SRHB. 10 & 13
TRANSMITTANCE
WAVENUMBER

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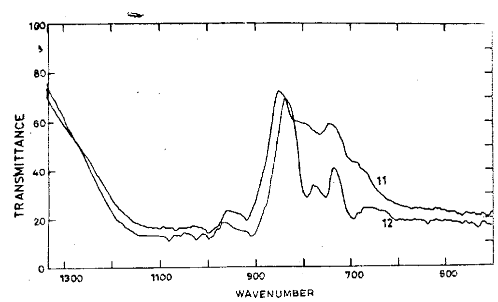
TRANSMITTANCE
WAVENUMBER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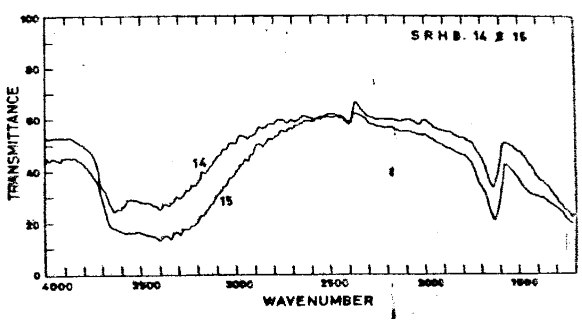
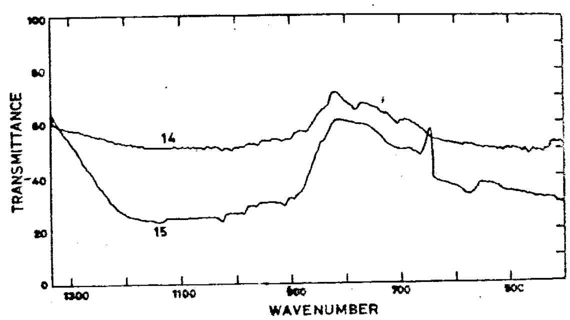
WAVENUMBER


SRHB. 14 & 15
TRANSMITTANCE
WAVENUMBER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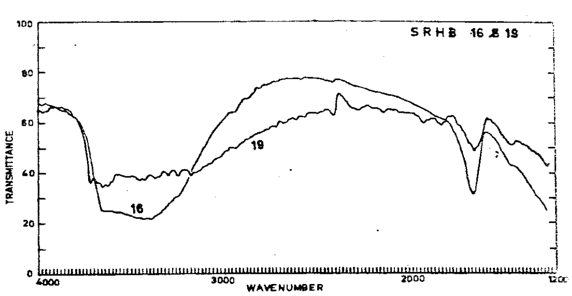
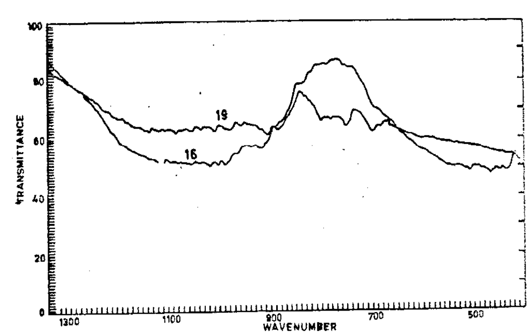
WAVENUMBER


SRHB 16 & 19
TRANSMITTANCE
WAVENUMBER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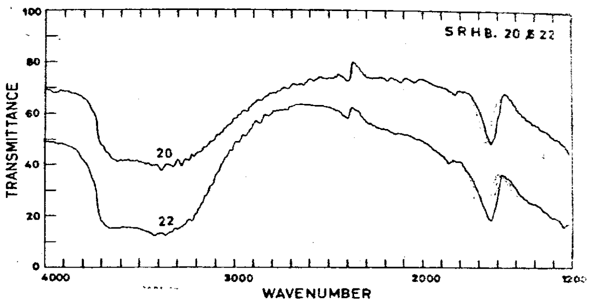
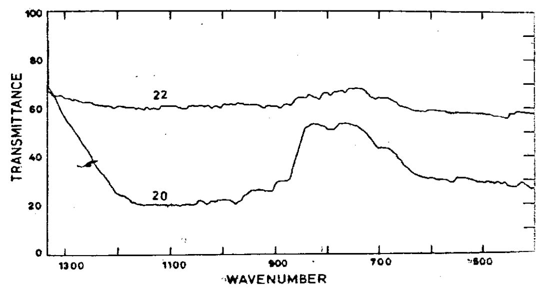
WAVENUMBER




## RESULTS AND DISCUSSION

### Infrared Studies

Hertzberg [19] and Barnes *et al*. [20] have shown the utility of IR spectra in mineralogy. Buswell *et al.* [21] showed that the absorption range 3700 $cm^{-1}$ is due to hydroxyl group in dioctahederal mineral each pair of $Al^{3+}$ ions have two hydroxyl groups which are related by centre of symmetry between $Al^{3+}$ ions. Farmer and Russel [22] stated that coupling between the vibrations of the two hydroxyl groups can give two frequencies of vibrations in which the two OH groups are out of phase (IR center) and in phase vibrations (IR inactive). The anti-symmetry in the region of small band at 3675 $cm^{-1}$ but weak band at 3647 $cm^{-1}$ could rise from symmetric vibrations (of which the symmetry is not ideal). In general substitution of magnesium and/or iron or aluminium in octahederal position tends to cause a broad absorption band in frequency region with a maximum of lower frequency. So far the question of Montmorillonite is concerned the absorbed water shows absorption at 3400 $cm^{-1}$ and another band around 1640 $cm^{-1}$.

These two bands correspond to deformation vibration of water. The strong vibration band between 3600 $cm^{-1}$ and 3700 $cm^{-1}$ is correlated to structural OH groups and absorption band at 915 $cm^{-1}$ indicates the influence of iron in the structure of Montmorillonite.

Farmer and Russel [22] described the lattice vibration in the region 1150 $cm^{-1}$ and 400 $cm^{-1}$. In this range the layer silicates in which $Al^{3+}$ for silicate substitution is absent or low give the sharp spectra, the two suggests in plane vibrations occur in the frequency range 1037 – 1018 $cm^{-1}$. The third high frequency in the plane vibration in the 1150 – 900 $cm^{-1}$ is reported to occur within relatively narrow range from 1121 – 1100 $cm^{-1}$. The absorption band when correlated with literature confirms the presence of Montmorillonite as major clay mineral in the Bentonite minerals of Rajmahal hills.

### X Ray studies

X ray method of Brindlays obtained from spacings less than 1 Å and therefore with copper $K_{\alpha}$ radiations, it was necessary to extend the camera to values of $2\Theta$ greater than 90°.

In the case of Monmorillonite belonging to Smactite groups of clay mineral basal spacings vary with the humidity of the atmosphere to which they are subjected. It became necessary to control the humidity of the atmosphere within the camera. Two types of imperfections of crystals used to be discussed, one may be due to highly symmetrical arrangement of the atoms in the various layers and the relatively weak binding force between them; the layers may be displaced with respect to one another. But the geometry of adjacent sheets of atom in contact remains the same; although the geometrical relation between the sheets of more distance atoms is changed. The result of such imperfection is the absence of certain types of reflections. Two dimensional diffraction effects become the major features when the layers are displaced randomly in two different directions.

Another kind of imperfection is found when layers of different types are interstratified. Many clay mineral layers are very similar because they are composed by silica tetrahedral sheets and closely packed layers of hydrogen and hydroxyls. They can be interstratified to bind structure and stabilise as structures composed of single layer. When the attraction of single layer is irregular, new diffraction defects arise. The shape and size of the crystal particle exposed to X ray also influence the diffraction effects.

The diffraction shown by powder diagram of smactite group of mineral can be classified in two categories; one consisting of basal reflections varying with state of hydration mineral, that is, with the thickness and hydration of water layers between the silicate sheets; the O-axis species, the differences of reflections and the number of order shown vary from sample to sample, depending on the thickness of water layers and their regularity; which factors in turn are dependent on exchangeable cation present and the condition under which the sample has been prepared because of variability of basal spacing they can be of no use in identifications.

The another type of diffraction consisting of general diffraction characteristics of the structure of Smactite layer themselves and are not dependent on interlayer hydration, these are h-k bands by using oriented aggregations as Mac Evan [23] has suggested patterns which contains the h-k lines can be obtained by suitably mounting to spacings in front the X ray beam.

The d values of X ray powder data of Bentonite minerals of Rajmahal hills are tabulated in Table 3 along with literature values and calculated X ray powder data of Montmorillonite and Kaolinite for comparison. On observation of these data it may be stated that the Montmorillonite clay mineral is present in all the samples along with Kaolinites in small proportions and Smactites in very small proportions [24].

**DTA and TGA studies**

After the consultation of the works of Bradley [25], Speil [26] and Grim [27], the differential thermal analysis curves of Bentonite of Rajmahal hills are presented in the Figure 2. The corresponding data of endothermic and exothermic peaks are recorded in the Table 4. The literature value for composition from Guha and Sen's paper [28, 29] are also given in Table 4.

The literature curve for Bihar Bentonite has been characterized by three endothermic effects, a large one at 145 °C, a medium one at 580 °C and a small one at 712 °C, as well as by a sharp exothermic at 980 °C. In case of Bentonite under study the characteristic peak below 225 °C is available at 189 °C (small), 218 °C (large), 170 °C (large), 221°C (medium), 207 °C (large), 140 °C (medium), 186 °C (medium) and 148 °C (small) in the case of SRHB – 1, 3, 4, 5, 6, 7, 9 and 19 respectively. Large endothermic peak at lower temperature indicated Montmorillonite type mineral in Bentonite.

The high temperature endothermic peak between 550 °C and 750 °C in the literature resulting from the lattice water showed a dual nature at 580°C followed by another at 712 °C. Dual is due to a mixing of high iron and high alumina varieties of Montmorillonite or due to the presence of a small amount of Kaolinite in a predominantly Montmorillonite clay. But in the case of Bentonites studied here the endothermic peaks at 567 °C ( large), 524 °C ( large sharp), 556 °C ( medium) and 582°C ( large), for SRHB – 1, 6, 7, 9 and 19 respectively have been shown separately. The endothermic peaks due to water appearance in the region 100°C to 300°C, and those for removal of structural hydrolysis in the region 900 to 950°C may be expected due to crystallization of new phase from anhydrous Montmorillonite. No endothermic peak in the region 900 to 950°C is being seen in the case of Bentonites for which DTA data have been reported in the Table 4.

The endothermic peaks at 950°C (medium) 912°C (small broad), 918°C (small), 927°C (small broad), 806°C (small broad) for SRHB 1, 4, 7, 9, 19 respectively are also observed.

Thermogravemetric curves for all these samples for which DTA curves have been shown, are presented in Figure 2. The corresponding data are presented in Table 4. It is clear from this table that the percentage loss in weight by SRHB – 1 is 18.83 percent which is more than 15.36 percent loss in weight for this sample obtained by common experiment of heating, cooling and weighing to constant weight. The percentage loss in weight by the sample SRHB – 3,4,5,6 obtained from DTG curves is slightly less than that obtained in the case of these samples by common experiment. But in the case of SRHB – 7, 9 and 19 the percentage loss in weight values are slightly higher than that obtained by common experiments. The lower temperature peak in each case is due to the removal of absorbed water, the second higher temperature peak is due to either removal of water associated with the interlayer ions.

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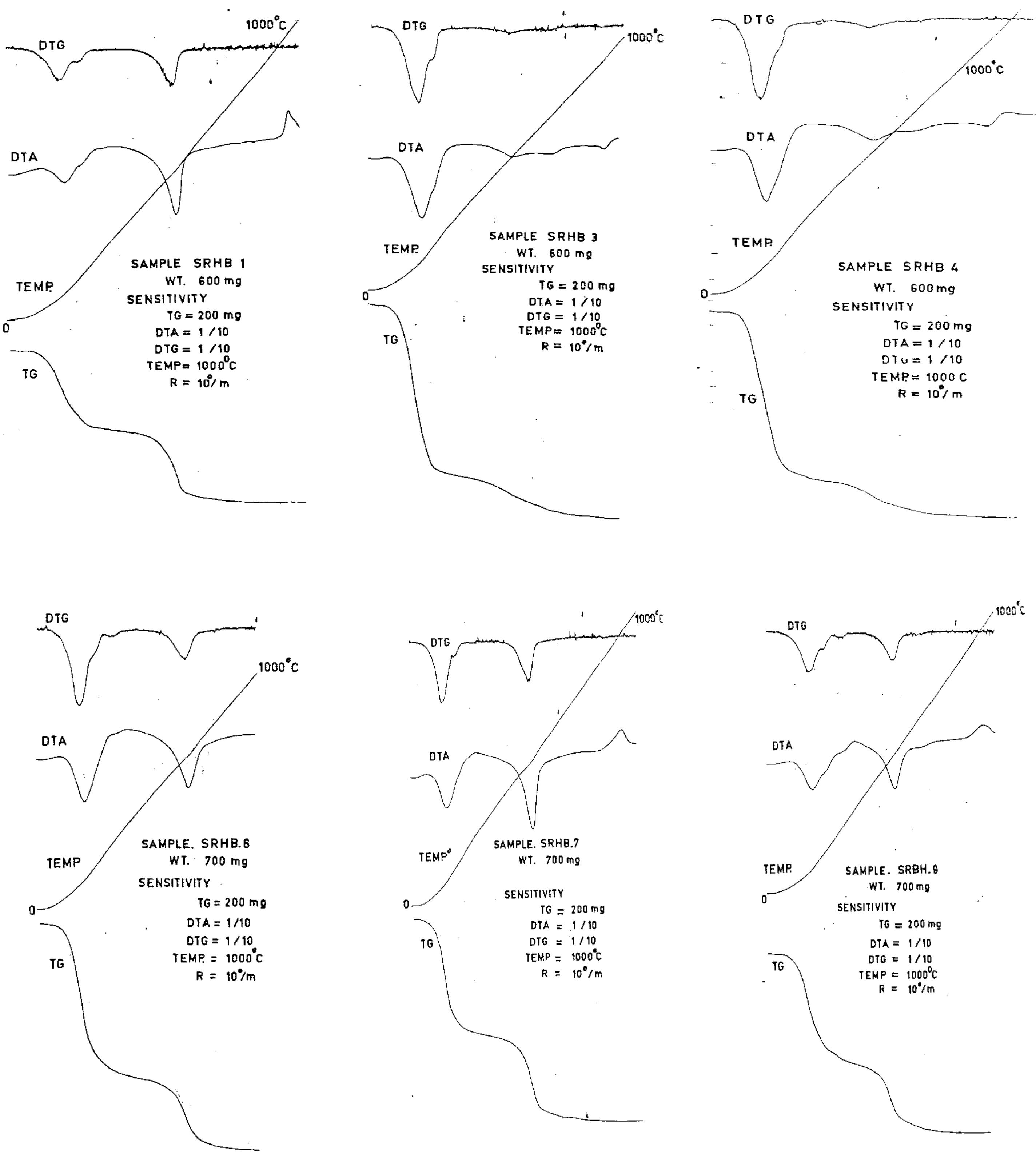
**Figure 2: DTA, TGA & TG Curves of Bentonite Minerals of Rajmahal Hills**



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