MINERALOGICAL CHARACTERIZATION STUDIES ON UNBURNT CERAMIC PRODUCT MADE FROM ROCK RESIDUE ADDITIVES BY FT-IR SPECTROSCOPIC TECHNIQUE

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Received (16 October 2012)

Revised (28 December 2012)

The usability of waste rock (rock residue) powder as an additive material in ceramic samples was investigated. Qualitative analysis was carried out to determine the major and minor constituent minerals present in ceramic bodies made from rock residue powder by using FT-IR spectroscopic technique. Further, the representative ceramic bodies are analyzed by FT-IR technique to yield more information about the functional groups and also to estimate the order or disorder of kaolinite structure.

Keywords: FT-IR Analysis; Rock Residue; Ceramic product.

Introduction

Rock waste such as residue powders which result from cutting, polishing, crushing and machining operations in the rock quarries have a significant and serious impact on the environment. The rock waste is potentially pollutant¹ although only a small part of it is correctly discarded. Most of rock waste is illegally dumped in land and in the environment. This practice causes negative effects on the environment and human health, since the fine powder in suspension can be inhaled^{2, 3}. The amount of powdery rock waste is estimated to be in the range of 20-25% of total production⁴.

The present research work is on the use of the waste material (rock residue) for manufacturing ceramic product. The main objective of this work is to identify and characterize the various minerals present in the ceramic products made from rock residue powder. Also to study, the order and disorder form of clay minerals and structural information about the ceramic samples using FT-IR Spectroscopic technique.

Experimental

A typical ceramic body formulated using a rock residue in the form of powder was selected as one raw material and mixture of another raw material is fire clay. The rock residue powder collected from a private rock-crushing plant located in Thuraiyur, Trichy district of Tamil Nadu, India and fire clay material collected from Govt. Ceramic institute, Virdhachalam of Tamilnadu.

The raw materials, Rock residue powder and fire clay material were dried and ground in an agate mortar. The various proportion of rock residue powder 0%, 10%, 20%, 30%, 40% & 50% were mixed with Fire clay material by weight basis. The green ceramic bodies were moulded into ASTM standard rectangular bars using a uniaxial pressing technique. After forming, the ceramic body specimens were dried in open atmosphere (3 days) and then in an oven dried for 24 hours at 110 °C. Six experimental ceramic bodies were named RW0, RW10, RW20, RW30, RW40 and RW50.

The rock residue powder mixed ceramic bodies (RW0-RW50) were well ground into a fine powder using agate mortar. The powder form Ceramic samples (RW0-RW50) were used for spectral studies involving FTIR

The infrared spectra were recorded in the mid IR region 4000-400 cm⁻¹ using Perkin Elmer FTIR interferometer in Centralized Instrumentation Sophisticated Laboratory (CISL), Annamalai University. The KBr pressed pellet technique was used by mixing the powdered samples with KBr in weight proportion of 1: 20. The precision of the FTIR instrument is ± 4 cm⁻¹ in 4000 to 2000 cm⁻¹ region and ± 2 cm⁻¹ between 2000 and 400 cm⁻¹.

Results and Discussion

The clay minerals are the essential and basic raw materials for making ceramic products. Knowledge of the structure of the clay material goes along way in characterizing the quality of such materials. Of the various well known methods of analysis, infrared spectroscopic is found to be a potential tool in investigating the structure of clay mineral⁵.

The FT-IR spectra of rock residue additives mixed Ceramic body specimens (RW0 - RW50) are shown in Fig. 1 and the absorption frequencies of the peaks in the spectra of each sample in the wave number (cm^{-1}) and present mineral name are reported in Table 1.

Table 1 shows the FT-IR spectral results of the Ceramic bodies from different proportions of rock residue mixture indicate the presence of Clay minerals (Kaolinite and Montmorillonite), Quartz, Hematite, Microcline (Feldspar) and Calcite. These minerals were identified by referring the reports in the literatures⁵⁻²⁵.

The FT-IR spectra of rock residue powder mixed Ceramic bodies RW0, RW10, RW20, RW30, RW40 and RW50 is shown in Figure 1 and the peak positions of various band of varied intensity observed in the spectra along with their tentative vibrational assignments are given in the Table 2. The intensity of bands varies from sample to sample which indicates its quantity.

Fig.1. FT-IR Spectra of Ceramic bodies made from rock residue (0-50 wt. %) additives

The around 3694 cm^{-1} strong band arises from the in phase symmetric stretching vibration of the OH groups, either outer or inner -surface OH of the octahedral sheets, which form weak hydrogen bonds with the oxygens of the next tetrahedral layer⁶. On the other hand, the near 3620 cm^{-1} strong band is due to the stretching vibrations of the "inner OH groups", lying between the tetrahedral and the octahedral sheet⁷.

It has been pointed out by Keeling⁸ that the bands at 3690 cm^{-1} and 3620 cm^{-1} can be attributed to outer and inner hydroxyl groups.

The IR spectra of the samples RW0, RW10, RW20, RW30, RW40 and RW50 show sharp absorption band around 3696 cm^{-1} which indicates the O-H stretching of kaolinite⁹ present in them.

A sharp absorption band observed 3620 cm^{-1} with strong to very strong intensity present in all the samples due to the O-H stretching of inner hydroxyl group⁸⁻¹⁰.

IR Spectra of all the clay minerals are very nearly similar indicating that the constituents are almost the same. Hence, Keeling⁸ pointed out the clay minerals can be characterized by general formula.

Where, the value of n lies between 0 to 1. One of the features of this series is that the proportion of outer (OH) groups decreases as n increases. The main features of the clay minerals absorption spectra are (i) the hydrogen bonding of the structural OH groups and (ii) Si-O and Al-O vibration in the tetrahedral and octahedral sub layers and other associated oxide minerals.

Table 1. Mineral constituents⁵⁻²⁵ in the rock residue mixed Ceramic bodies (RW0-RW50)

Mineral Name	IR absorption band (cm ⁻¹)					
	RW0	RW10	RW20	RW30	RW40	RW50
Clay Mineral (Kaolinite & *Montmorillonite)	3696 sh & M	3696 V.S	3696 sh & V.S	3696 sh & V.S	3696 sh & V.S	3692 sh & S
	3673 M	3673 S	-	-	-	-
	3668 M	3668 S	3668 S	3669 sd & S	3669 S	3670 sh & M
	3654 M	3654 sh & S	3654 S	3652 sh & S	3651 sh & S	3651 sh & S
	3648 M	-	-	-	*3448 W	*3460 bd & W
	3620 sh & S	3620 sh & V.S	3620 sh & V.S	3620 sh & V.S	3620 sh & V.S	3620 sh & S
	-	1628 sd & W	-	1629 V.W	-	-
	1634 V.W	-	1636 bd & V.W	1636 V.W	1638 bd & V.W	1635 V.W
	1116 S	1116 sh & V.S	1115 sh & V.S	1116 sh & V.S	1114 sh & V.S	1115 sh & V.S
	1031 V.S	1033 V.S	1031 bd & V.S	1032 bd & V.S	1031 bd & V.S	1033 bd & VS
	1006 V.S	1003 V.S	1006 bd & V.S	1006 bd & V.S	1006 bd & V.S	1006 sh & V.S
	912 sh & S	913 sh & V.S	912 sh & VS	912 sh & VS	912 sh & W	912 sh & VS
	428 S	432 sh & S	429 sh & M	431 S	431 sh & M	431 sh & W
	-	424 sh & S	-	427 S	-	-
Quartz	794 W	795 sh & M	793 sh & W	793 sh & M	793 sh & W	794 sh & W
	694 W	695 sh & M	695 sh & M	695 sh & M	695 sh & M	695 sh & W
	467 S	469 V.S	466 sh & V.S	468 sh & V.S	468 sh & V.S	468 sh & M
	-	465 V.S	-	-	-	-
Hematite	538 S	534 sh & V.S	539 sh & V.S	537 sh & V.S	536 sh & V.S	539 sh & S
Microcline	-	648 W	-	-	-	-
Calcite	1825 V.W	1822 V.W	1830 V.W	1819 V.W	1822 V.W	1823 V.W

Ramaswamy and Kamalakkannan⁵ observed that the ratio of the intensities of 3690 cm^{-1} to 3620 cm^{-1} band that this ratio is ≈ 1 in the case of well order clay mineral while it 0.25 in disorder ones. This ratio is a measure of the degree of disorder and can be correlated with the hydroxyl deficiency.

According to Russell¹¹ and Ramasamy *et al.*^{12, 13}, if four peaks are observed in the region $3697\text{--}3620\text{ cm}^{-1}$, the minerals are said to be ordered state. However, in the present study four peaks are observed at (near) 3696 cm^{-1} , 3668 cm^{-1} , 3651 cm^{-1} and 3620 cm^{-1} in some samples (RW20–RW50). This suggests the minerals may be in order state and the IR Spectra of these samples with four peaks between the ranges from 3696 to 3620 cm^{-1} reflecting the crystalline order of Kaolinite is shown in Fig. 2. Farmer & Russell¹⁴ and Miller¹⁵ assigned the

absorption band at 3620 cm^{-1} as due to hydroxyl group on the side of the tetrahedral sheet.

Fig. 2. FT-IR Spectra of ceramic samples with four peaks between the ranges from 3696 to 3620 cm^{-1} reflecting the crystalline order of Kaolinite.

The sample RW0, RW10 and RW40 which show the absorption

band positioned $3569\text{--}3565\text{ cm}^{-1}$ and 3460 cm^{-1} may be assigned to H-O-H vibration of adsorbed water¹⁶ and the presence of weak shoulder bands at 3586 cm^{-1} , 3544 cm^{-1} and 3537 cm^{-1} are attributed to O-H stretching of water coordinate to Al, Mg. The characteristics bands observed 3448 cm^{-1} and $1628\text{--}1638\text{ cm}^{-1}$ is attributed to O-H stretching and H-O-H bending of adsorbed water molecules^{16, 17}.

Lara Maritan *et al.*¹⁸ and Colombini *et al.*¹⁹ have reported that two weak peaks observed at 2852 cm^{-1} and 2922 cm^{-1} are due to C-H stretching mode and reveal the presence of some organic contribution. The IR peaks corresponding range $2922\text{--}2926\text{ cm}^{-1}$, 2853 cm^{-1} and 2954 cm^{-1} is due to C-H stretching of organic matter^{18, 19} present in all the ceramic bodies. IR spectra of rock residue powder mixed ceramic samples (RW0–RW50) shows the presence of very weak absorption band $1880\text{--}1887\text{ cm}^{-1}$ and this band indicates the presence of calcite stretching vibration²⁰.

The infrared absorption bands at (around) 1620 cm^{-1} has been assigned to H-O-H bending of water¹⁶.

All the ceramic samples give very strong band in the region $1100\text{--}1000\text{ cm}^{-1}$ which is characteristic of silicate minerals.

Ghosh²¹ has stated that the position of the silicate band with the intense absorption at 1030 cm^{-1} indicates red clay origin and around 1070 cm^{-1} due to white clay origin. If the absorption band is observed around 1040 cm^{-1} , it is probably due to the mixture of both red and white clay origin. In case of all the samples have silicate band is found to be centered around 1030 cm^{-1} with very strong intensity indicating red clay origin of the kaolinite clay used in making the ceramic product^{22, 23}.

In the present IR spectra, three important absorption bands are observed (near) 1114 cm^{-1} , $1003\text{--}1006\text{ cm}^{-1}$ and $1030\text{--}1033\text{ cm}^{-1}$ for ceramic samples (RW0–RW50). The very

Table 2. FT-IR Spectroscopic results of rock residue powder mixed Ceramic bodies

RW0	RW10	RW20	RW30	RW40	RW50	Tentative vibrational assignment
3696 sh & M	3696 V.S	3696 sh & V.S	3696 sh & V.S	3696 sh & V.S	3692 sh & S	O-H stretching of hydroxyl sheet
3673/3668 M	3673/3668 S	3668 S	3669 sd & S	3669 S	3670 sh & M	O-H Stretching of inner-surface hydroxyl group
3654 / 3648 M	3654 sh & S	3654 S	3652 sh & S	3651 sh & S	3651 sh & S	
3620 sh & S	3620 sh & V.S	3620 sh & V.S	3620 sh & V.S	3620 sh & V.S	3620 sh & S	O-H stretching inner hydroxyl group
3586 sd & W	-	-	-	-	-	O-H stretching of water co ordinate to Al, Mg
3565 sd & W	3566 sd & M	-	-	3569 sd & W	-	H-O-H adsorbed water
-	3544 sd & W	-	-	3537 W	-	O-H stretching of water co ordinate to Al, Mg
-	-	-	-	-	3460 bd & W	H-O-H adsorbed water
-	-	-	-	3448 W	-	O-H stretching of water
2922 V.W	2925 V.W	2925 sh & V.W	2926 V.W	2926 V.W	2923 V.W	C-H Stretching of organic matter
2853 V.W	2854 V.W	2853 sh & V.W	2854 V.W	2854 V.W	2854 V.W	C-H Stretching of organic matter
1825 V.W	1822 V.W	1830 V.W	1819 V.W	1822 V.W	1823 V.W	Calcite stretching vibration
1634 V.W	1628 sd & W	1636 bd & V.W	1629 /1636 V.W	1638 bd & V.W	1635 V.W	H-O –H adsorbed water
-	-	-	1653 V.W	-	-	O-H deformation of water [Al-O-(OH) ₆]
1116 S	1116 sh & V.S	1115 sh & V.S	1116 sh & V.S	1114 sh & V.S	1115 sh & V.S	
1031 V.S	1033 V.S	1031 bd & V.S	1032 bd & V.S	1031 bd & V.S	1033 bd & VS	Si –O of stretching
1006 V.S	1003 V.S	1006 bd & V.S	1006 bd & V.S	1006 bd & V.S	1006 sh & V.S	Si –O of stretching
912 sh & S	913 sh & V.S	912 sh & VS	912 sh & VS	912 sh & W	912 sh & VS	Al-(OH)
794 W	795 sh & M	793 sh & W	793 sh & M	793 sh & W	794 sh & W	Si –O of quartz
754 V. W	755 sh & W	754 sh & W	754 sh & W	754 sh & W	755 sh & W	Al-O-Si
694 W	695 sh & M	695 sh & M	695 sh & M	695 sh & M	695 sh & W	Si –O of quartz
-	648 W	-	-	-	-	Si-O-Al
538 S	534 sh & V.S	539 sh & V.S	537 sh & V.S	536 sh & V.S	539 sh & S	Fe –O of Fe ₂ O ₃
467 S	469/465 V.S	466 sh & V.S	468 sh & V.S	468 sh & V.S	468 sh & M	Si-O-Si bending of silicates
428 S	432 / 424 sh & S	429 sh & M	431 / 427 S	431 sh & M	431 sh & W	Si –O of mixed vibration

strong broad band, near 1114 cm^{-1} , is due to $[\text{Al-O}(\text{OH})_6]$. This band is investigated by Percival et al.¹⁰. The $1003\text{--}1006\text{ cm}^{-1}$ and $1030\text{--}1033\text{ cm}^{-1}$ band is attributed to the Si-O stretching vibration present in all ceramic samples. From the FTIR study, the absorption bands at 912 cm^{-1} and 913 cm^{-1} is due to Al-(OH) vibrations^{10, 24} present in all the ceramic samples.

According to Miller¹⁵, the well order clay minerals are characterized by the presence of 920 cm^{-1} , 1120 cm^{-1} and 1030 cm^{-1} band. The many reasonable IR peaks (near 1114 cm^{-1} , 1030 cm^{-1} & 910 cm^{-1}) are present in all the ceramic samples. This indicate that the well order of clay mineral structure.

All these samples show the absorption band of $793\text{--}795\text{ cm}^{-1}$ and near 694 cm^{-1} which are attributed of Si-O modes of quartz¹¹. The weak IR absorption bands are attributed at 754 cm^{-1} and 755 cm^{-1} . These bands indicate that Al-O-Si inner surface vibration²⁵ is present in all the ceramic samples.

According to Ellass and Oliver²⁶, the presence of the sharp band at 694 cm^{-1} indicates thin particles and in this case of thick particle, this band would shift to 689 cm^{-1} . Since all the ceramic samples show this band at 694 cm^{-1} & 695 cm^{-1} it is clear that all these samples contain quartz of thin particle size. The many authors^{27, 28} are reported the quartz with small (thin) particle size, improves mechanical strength. By contrast, large size particles tend to decrease the mechanical strength due to micro-crack formation.

According to Lyon²⁹, the IR peaks at $648\text{--}641\text{ cm}^{-1}$ are diagnostic of microcline. Since IR spectra of the sample (RW10) shows the infrared absorption peak in the range of 648 cm^{-1} it indicates the presence of microcline form of feldspar. This band does not appear in all samples (except RW10) and indicates the absence of microcline.

All the samples show very strong absorption peak around 535 cm^{-1} they are due Fe-O of Fe_2O_3 (hematite). This band shows that the crystalline hematite mineral^{21, 30}.

The bands at $465\text{--}469\text{ cm}^{-1}$ and $424\text{--}432\text{ cm}^{-1}$ have assigned to Si-O-Si bending and Si-O mixed vibration mode^{31, 32} present in all the ceramic samples.

Conclusions

The results presented and discussed along this report enable the following conclusions to be drawn:

- The qualitative mineral identification of ceramic bodies was carried out by FT-IR Spectroscopic technique.
- The FT-IR spectral analysis of Ceramic bodies from different proportions of rock residue mixture indicate the presence of Clay minerals (Kaolinite and Montmorillonite), Quartz, Hematite, Microcline and Calcite.
- All the samples studied in the present investigation are order form of Kaolinite (clay minerals).
- The bands at near 3696 cm^{-1} and 3620 cm^{-1} assigned outer and inner hydroxyl stretching vibration of the Kaolinite structure is present in all the ceramic samples made from rock residue.

- The presence of Aluminium and iron groups are indicated by the absorption peaks near 912-913 cm^{-1} and 534-539 cm^{-1} .
- The 694 and 695 cm^{-1} peak absorption is the indication of quartz particle present in the sample as thin (small) size. This quartz with small particle size, improves mechanical strength of the ceramic bodies.
- It is important to note that FT-IR spectra obtained for pure clay ceramic body sample (RW0) as well as rock residue mixed ceramic body samples (RW10-RW50) are almost identical.

The present study demonstrates usefulness of spectroscopic techniques in determining quality of ceramic samples made from 10-50 wt. % of rock residue additives.

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