

## Regular Article

## FT-IR Technique in Marine Sludge Studies

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**Abstract**

FT-IR spectroscopy is a quick and useful method to monitor the sludge process: however any particular sludge mixture needs preliminary studies of the spectra. The FT-IR technique was used to distinguish between different types of organic contents and to derive information concerning their composition and structural changes upon chemical modification. No special accessories were used: the reported sampling technique is commonly available in the infrared laboratories. The selection of the sampling technique used depends 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 sludge during heat treatment. The study then reviews the major scientific and technological advances, focusing principally on the developments in raw materials compositions resulting from the introduction of certain key raw materials to enhance composition quality. As the interpretations of unfired marine sludge compositions and the relation of fired marine sludge compositions have drawn particular attention from the scientific community, the paper addresses these issues in depth.

**Keywords:** FT-IR Spectroscopy, Marine sludge, Thermal analysis**Introduction**

Marine Sludge contains harmful heavy metals and organics which are dangerous for human and marine organism. This marine sludge settled in the sea floor poses real problems for both environment and harbor operation. The sludge has been regularly removed from the harbor floor by excavation to create room for large tonnage ships to safely dock in the harbour. The sludge removed from the harbor must be safely kept in some form. Marine sludge is regarded as a suitable raw material for brick production because of its perpetual availability, homogeneity and mineralogical & chemical composition [4]. The use of the sediment as a clay mixture in brick manufacturing seemed possible up to 40% [2]. The management of this sludge is a major part of waste treatment involving substantial cost and effort.

A review of the literature on the use of marine sludge shows that it could be used as an additive compound in ceramic building materials [4]. According to the study by [3], the sludge dredged from izmir bay can be used up to 50% in brick production and the produced

brick containing 50% sludge additives by weight presented usable ceramic properties [3].

The motivation behind this work, which was inspired by the results of the above study, was on the use of marine sludge in ceramic ware production where environmentally hazardous chemicals would be immobilized within a vitrified ceramic body. The targeted ceramic could be a tile. Although extensive research have been conducted on the use of sludge in brick production. A study on the sludge containing tile production is limited.

Ceramic tile can be defined as inorganic, non-metallic materials [8]. They are typically crystalline in nature and are compounds formed between metallic and non-metallic elements such as Aluminium and Oxygen (Alumina-  $\text{Al}_2\text{O}_3$ ), Calcium and Oxygen (Calcium CaO), and Silicon and Nitrogen (Silicon Nitrate  $-\text{Si}_3\text{N}_4$ ), ceramic materials are rock or clay mineral materials clay is the vital raw material to be used in ceramic industry.

Ceramic tiles are materials of variable porosity, composed essentially of clays and other inorganic raw materials such as quartz, iron oxides and carbonates. In the fabrication process, the raw materials are mixed in proportions taking into account the influence of each component in the properties of the final materials, followed by general processing steps such as pressing and firing. Common components that play fundamental roles for optimum processing, and hence performance of the final products, are kaolin or kaolinite clay for plasticity, feldspar for fluming and silica as filler material. In the processing steps, sintering of the ceramic masse is fundamental to adjust several derived properties and occurs in general through liquid-phase formation, these the presence of components such as low-melting clays is very important [9].

For the present study, an attempt has been made to subject the ceramic tile powder with different proportion of marine sludge. To identify the minerals constituent the FT-IR spectra were recorded.

**Materials and Methods**

The marine sludge was collected from Cuddalore harbour region. In the collected ceramic tiles powder (Government Ceramic Institute, Virudhachalam) was added for various concentrations (0% - 50%). So, seven samples ( $S_0$ - $S_6$ ) have been prepared in different proportions as given below in the table.

Sample No.	$S_0$	$S_1$	$S_2$	$S_3$	$S_4$	$S_5$	$S_6$
Ceramic tiles powder(Masse)	0%	100%	90%	80%	70%	60%	50%
Marine sludge	100%	0%	10%	20%	30%	40%	50%

A small amount of the sample (~1mg) was mixed with some finely ground potassium bromide (~20mg) in an agate mortar. The mixture was placed in a 13mm diameter die cavity and pressed under vacuum at a pressure of 8 tones. The disc was dried over night at 120°C to remove any traces of adsorbed moisture. The infrared spectrum of the sample between  $4000\text{cm}^{-1}$  and  $400\text{cm}^{-1}$  was then automatically recorded in the form of a chart using a Nicolet Avatar – 360 Serious FT-IR Spectrometer.

**Result and Discussion****Mineralogy of the raw material ( $S_0$  and  $S_1$ )**

The FT-IR spectra of  $S_0$  and  $S_1$  in the received state were presented in the figure 1.1. The absorption observed in the spectra with their relative intensity, minerals name and tentative assignment and tabulated in table 1. It is seen from the spectra of their both the samples of raw material  $S_0$  and  $S_1$  (sludge and masse) are slightly different.

In the studies of clay minerals the absorption bands due to structural OH and Si-O groups play frequently an important role in the differentiation of clay minerals from each other. To provide a routine characterization of a clay mineral, it is useful to examine a sample measured in a KBr disk. Two sample concentrations are usually needed to record optimal spectra over the range  $4000\text{cm}^{-1}$ -

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400 $\text{cm}^{-1}$ . Two to three milligrams of the sample dispersed in 200mg of KBr permit detailed examination of the OH stretching region, while the region below 1200  $\text{cm}^{-1}$ , where intense Si-O absorptions and OH bending bands are present, requires less than 1 mg of the sample.

FT-IR spectroscopy is a useful tool to evaluate the formation of new Al-O/Si-O bonds from raw materials in order to evaluation of ceramic process. With the help of FT-IR spectroscopy, poor crystalline and amorphous component can be identified. And IR spectroscopy was also extensively used to investigate organic substance in ceramic specimens.

Figure 1 shows the KBr spectra of  $S_0$  and  $S_1$  differing in the stacking arrangements of their clay minerals sheets, as well as in the

occupancy of the octahedral and tetrahedral sites. Kaolinite with mostly Al in the octahedral positions has four absorption bonds in the OH stretching region (figure 1). Inner hydroxyl group, lying between the tetrahedral and octahedral sheets, give the absorption near 3620  $\text{cm}^{-1}$ . The other three OH groups reside at the octahedral surface of the layers and from weak hydrogen bonds with the oxygen's of the Si-O-Si bonds on the lower surface of the next layer. A strong band at 3696  $\text{cm}^{-1}$  is related to the in-phase symmetric stretching vibration, two weak absorptions at 3669 and 3650  $\text{cm}^{-1}$  are assigned to out-of-plane stretching vibration [7]. The absorption near 3620  $\text{cm}^{-1}$ , similarly as for kaolinite, is assigned to the inner hydroxyl-group.

Fig1.1: FT-IR spectra of marine sludge ( $S_0$ ) and masse ( $S_1$ )

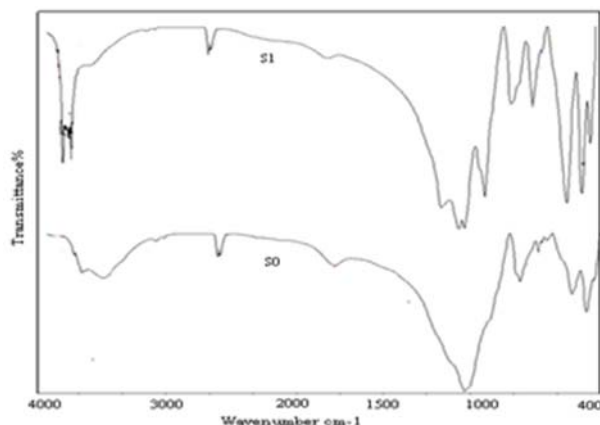


Table: 1 Infrared absorption frequencies ( $\text{cm}^{-1}$ ) for marine sludge ( $S_0$ ) and masse ( $S_1$ )

$S_0$ sludge	Int.	$S_1$ masse	Int.	Tentative assignments	Corresponding minerals
3690	v.w	3696	s	OH stretching internal surface free ( $\text{Al}_2\text{O-H}$ )	Kaolinite
-	-	3676	v.w	-	-
-	-	3669	v.w	Deformation internal surface free OH ant symmetric mode ( $\text{Al}_2\text{O-H}$ )	Kaolinite
-	-	3650	m	-	-
3619	v.w	3620	s	O-H stretching of inner hydroxyl group	Kaolinite
3600	v.w	-	-	-	-
-	-	3568	v.w	FeFeOH	Nontronite
2924	w	2926	v.w	Organic matter	-
2852	v.w	2853	v.w	Organic matter	-
2361	m	2360	m	-	-
2343	w	2343	w	-	-
2272	v.w	-	-	-	-
1636	v.w.br.	1633	v.w.br	Stretching vibration of free hydroxyl group	(-)
-	-	1114	w	Si-O bond	-
1032	v.s	1031	m	Si-O of stretching	Kaolinite
-	-	1006	m	Si-O-Si symmetric stretch	Kaolinite
-	-	-	-	-	-
-	-	912	s	$\text{Al}_2\text{O-H}$ deformation (internal surface OH)	Kaolinite
-	-	793	s	Si-O of quartz	Quartz
778	m	-	-	-	-
694	m	694	s	Si-O- quartz	Quartz
669	w	-	-	-	Quartz
647	w	651	v.w	-	Feldspar
534	m	536	v.s	Si-O-Al <sup>iv</sup> (or) $\text{Fe}_2\text{O}_3$	Hematite
466	s	468	v.s	Si-O-Si bending	Quartz
432	v.w	430	s	Si-O of mixed vibration	-

V.S → Very strong; S → Strong; M → Medium; W → Weak; V.W → Very Weak; Br → Broad;

The vibration of two surface hydroxyls, forming stronger hydrogen bonds with the adjacent layer, are coupled and give a strong band at  $3650\text{ cm}^{-1}$ . The third layer-surface hydroxyls from weak hydrogen bonds and absorb at  $3700\text{ cm}^{-1}$  [7].

The position of the OH band at  $3567\text{ cm}^{-1}$  is characteristic for nontronites in which FeFeOH grouping dominates in the octahedral sheets. The OH stretching region of hectorite and saponite reflects their trioctahedral character with mainly  $\text{Mg}_3\text{OH}$  units in the octahedral sheet, absorbing near  $3680\text{ cm}^{-1}$ . Hectorite and saponite are difficult to distinguish from their spectra at first sight, however, some spectral details allow their identification [7]. On the other hand the intense Si-O and Si-O-Al stretching frequencies lying at  $1114\text{ cm}^{-1}$ - $1006\text{ cm}^{-1}$  are consistent with the spectra pattern of kaolinite, as well as doublet at  $934 - 913\text{ cm}^{-1}$  attributed to Al-OH libration. However, characteristic band belonging to quartz, feldspar, another clay are overlapping in the same region.

The sharp band at  $793$  and  $695\text{ cm}^{-1}$  is a diagnosis to identify quartz. In the low energy, below  $500\text{ cm}^{-1}$ , the vibration belonging mainly to deform of  $\text{SiO}_4$  and  $\text{AlO}_6$  polyhedra of all constituents are not generally valuable for diagnosis due to their coupling.

The comparison of both spectra shown in figure 1.1 allows differentiate certain components in the  $S_0$  and  $S_1$  specimens. In the case  $S_1$ , extra bands assigned to kaolinite and quartz are detected, although weak and strong at  $3669$ ,  $3650$ ,  $921$  and  $793\text{ cm}^{-1}$ .

The Si-O and Al-O deformation: a combined Al-O and Si-O deformation mode [2] is observed at about  $468\text{ cm}^{-1}$  in the IR spectra of the  $S_0$  and  $S_1$  (figure 1.1). The unfired raw materials ( $S_0$  and  $S_1$ ) showed in this spectral range three spectral deformation bands at  $430$ ,  $468$  and  $535\text{ cm}^{-1}$  (figure 1.1 and table 1). From the samples  $S_0$  and  $S_1$  these bands were assigned as Si-O, Si-O-Si and Si-O-Al deformation vibrations respectively [6].

It is found that both the two sample  $S_0$  and  $S_1$  are containing kaolinite as principal clay mineral. Almost both the two samples have quartz as secondary minerals both these samples  $S_0$  and  $S_1$  contain feldspar and hematite as accessory minerals.

#### Mineralogy of the fired samples ( $S_1 - S_6$ )

The infrared spectra of all specimens ( $S_1-S_6$ ) were compared. A comparison of the spectra of fired samples with that of unfired raw samples reveal that this firing step the bands at  $3700-3600\text{ cm}^{-1}$  are clearly modified due to dehydroxylation of kaolinite giving rise, as expected, to meta kaolin. It was also found that dehydroxylation between  $500$  and  $700^\circ\text{C}$ , is accompanied by amorphization since the aluminosilicate sheets are disrupted [10]. On the other hand, the most intense band centered at  $1000\text{ cm}^{-1}$  is slightly displaced (from  $1030\text{ cm}^{-1}$  into  $1085\text{ cm}^{-1}$ ) towards higher wave number reflecting the increasing of Si-O-Si, Al-O-Al bonds along with the formation of new Si-O-Al ones. The characteristic Al-OH libration mode at  $937-612\text{ cm}^{-1}$  is lacking. O-H stretching vibrations are highly sensitive to IR radiation. Thus, this is perhaps the most important and distinctive region of the spectra, because non-clay minerals have no hydroxyl groups in their structure. This absorption disappears completely after heat treatment over  $950^\circ\text{C}$  in most clay. The lack of OH bands of dehydroxylation occurring during calcinations is taken as direct evidence of amorphization [8].

The presence of anorthite was confirmed by FT-IR. The formation of anorthite during firing is postulated. From calcite thermal decomposition (likely present in the raw material) followed by co-reaction with clays. This hypothesis is spectroscopically demonstrated by the absence of highly sensitive IR carbonate bands, around  $1400\text{ cm}^{-1}$ .

Fig. 1.2: FT-IR spectra of ceramic tiles (raw) and fired at different temperature of sample  $S_1$

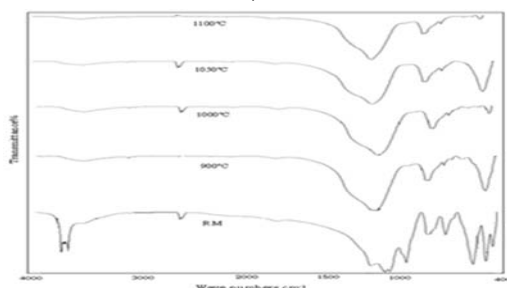


Fig. 1.3: FT-IR spectra of ceramic tiles (raw) and fired at different temperature of sample  $S_2$

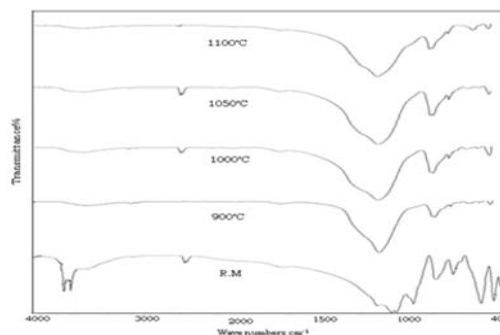


Fig. 1.4: FT-IR spectra of ceramic tiles (raw) and fired at different temperature of sample  $S_3$

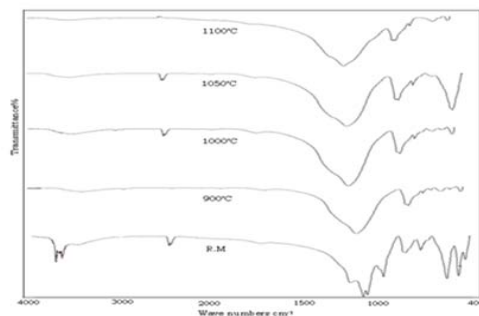


Fig. 1.5: FT-IR spectra of ceramic tiles (raw) and fired at different temperature of sample  $S_4$

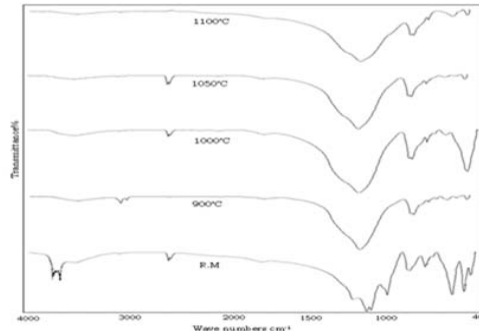


Fig. 1.6: FT-IR spectra of ceramic tiles (raw) and fired at different temperature of sample  $S_5$

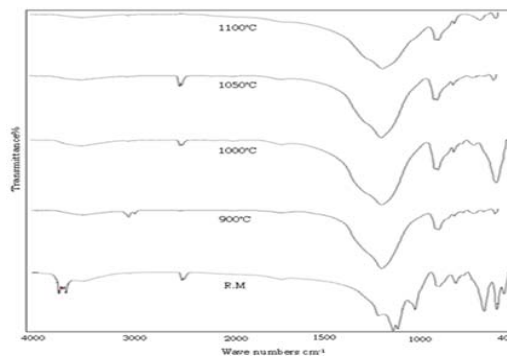
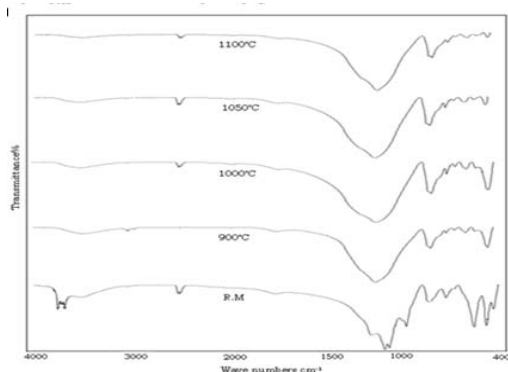


Fig. 1.7: FT-IR spectra of ceramic tiles (raw) and fired at different temperature of sample S<sub>6</sub>



The Al-O vibrations of anorthite are assigned to low intensity signals detected at  $\sim 600\text{ cm}^{-1}$  (adsorption at  $567$  and  $538\text{ cm}^{-1}$ ) [11]. Si-O vibrations from quartz are more clearly distinguishable, as shown in the figure, since it remains crystalline as in the raw material. This is observed as the sharp doublet  $797\text{--}780\text{ cm}^{-1}$ . The intense absorption at  $\sim 1100\text{ cm}^{-1}$  (Si-O stretching) is broad, as the doublet at  $\sim 500\text{ cm}^{-1}$  ( $\text{SiO}_4$  deformation) in the pure IR spectra is unresolved.

These features are also consistent with superposition with Si-O vibrations of the  $\text{SiO}_4$  condensed tetrahedral of fired clay layers (feldspar). The overall displacement forward higher energy of the intense band is consistent with the reinforcement of the Si-O bond of the main phases formed after long firing ( $1200^\circ\text{C}$ ). The enhancement in the broadness (figures 1.2-1.7) of this band forward its lower energy side may be also attributed to anorthite.

Mullite, the  $\text{Al}_2\text{O}_3$  – rich phase of  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$  system is considered the most important material developed during firing due to the improved thermo-mechanical properties.

Mullite formation has been extensively studied by FT-IR spectroscopy [11]. The sequence of phase transformation departing from amorphous clay aluminosilicate involves formation of Al-Si spiral precursor phase at  $\sim 1000^\circ\text{C}$  before crystal mullite. The temperature of formation is variable, depending upon the nature of the clay. Nevertheless, according to our spectra (figures 1.2-1.7), its presence is detected by the low intensity band. The most easily recognizable of the band at  $570\text{ cm}^{-1}$ , assignable to Al-O stretching in  $\text{AlO}_6$  of the spiral precursor of the mullite phase [11].

The loss of resolution in the  $900\text{--}400\text{ cm}^{-1}$  is due to the existence of agglomeration aluminosilicates (and perhaps of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) in the amorphous state.

At the firing treatment  $1100^\circ\text{C}$  bonds at  $587$  and  $535\text{ cm}^{-1}$  as may be seen in figure 1.2, are indistinguishable. They overlap into one broad absorption band centered around  $563\text{ cm}^{-1}$  assignable to  $\text{AlO}_6$ . Octahedral presented in mullite. The overlapping in broadness of Al-O band probably indicates a disordered distribution in this samples or short range order in the crystal structure [1].

Quartz is a residual mineral from the original raw materials, and mullite, formed during firing ceramic tile (sludge additive) the dehydroxylated kaolin, metakaolin, transforms into a non equilibrium unstable spinal type structure, which converts to mullite above

$1050^\circ\text{C}$  (figure 1.2). For the compositions containing sludge some modifications in intensity and position of the bands in the FT-IR spectra indicate the presence of anorthite, and the amount of which increase with increasing percentage of sludge.

## Conclusion

The results of this study of mineralogical transformations show the dependence of firing temperature on the properties of the two main types of raw materials (masse and sludge) from cuddalore marine area harbour site led to the following conclusions. Although the raw materials masse and marine sludge have been the same kaolinic predominance. It was suitable to prepare ceramic tiles from a marine sludge material up to 50 %. Raising the percentage above this value did not enhance the vitrification properties. (The presence of organic matter in sludge gives rise to the formation of microstructural crack dark spots and "black core" defects) the optimum firing conditions are  $1100^\circ\text{C}$  firing temperature. This is environmentally beneficial because the waste to be recovered and directly applied as a ceramic raw material at low-cost with energy saving and diminishing the environmental impact. However, further ceramic processing using the raw material studied in this work would improve upon the present results.

## References

1. Cheng, Y.F., Wang, M.Ch. and Hon, M.H., Phase transformation and growth of mullite in kaolin ceramics, *J. Eur. Ceram. Soc.*, 24 2389-2397 (2004).
2. Freund, F., In: V.C. Farmer (Ed.), the infrared spectra of minerals, mineralogical society, London, p.465, (1974).
3. Giese, L.B., Werit Z, F., Weimann, K., Niederleithinger, E and Ulbricht, J.P. "Bricks made of sludge from the Izmir bay an integrative approach for the recycling of sludge – preliminary results". Proceeding of the first international exergy, Energy & Environment symposium, Izmir (13-17 July 2003).
4. Hamer, K and Karius, V. "Brick production with dredged harbour sediments. An industrial scale experiment", *Waste management Vol.22*, pp. 521-530 (2002).
5. Karpuzcu M. Buktel, D. and Aydin, Z.S. "The devaterabilty, Heavy metal release & Reuse characteristic of golden Horn surface sediment". *Wat. Sci. Tech. Vol.34*, pp. 365-374 (1996).
6. Madejova, J. and Komadel, P., clay and clay minerals, 49, 410 (2001).
7. Madejova, J., FT-IR techniques in clay mineral studies; *Vibrational Spectroscopy*, 31, 1-10 (2003).
8. Raghavan, V., "Text book of material science & Engineering", Third edition prentice – Hall of India Private limited New Delhi – 110 001, (1995).
9. Sanchez-Munoz, L., Cava, S.S., Paskocimas, C.A., cerisuelo, E., Longo, E., Carda, J.B., Modelling of the vitrification process of ceramic bodies for ceramic tiles, *ceramic 48*,137-145 (2002).
10. Shvarzman. A., Kovler, K., Grader, G.S and Shter, G.E., The effect of dehydroxylation / amorphization degree on pozzolanic activity of kaolinite, *cem.conr.res.*,33,405-416 (2003).
11. Voll. D., Angere, P., Beran, A. and Schneider, H., A new assignment of IR vibration modes in mullite. *Vibration spectroscopy*30(82),237-243(2002).