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RESEARCH ARTICLE

FTIR AND MOSSBAUER STUDIES ON INDUSTRIAL CLAY BRICKS FROM THREE DIFFERENT REGIONS OF TAMILNADU STATE , INDIA

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ABSTRACT

The present study aims to estimate the firing temperature and firing condition of the industrial clay bricks from three different regions namely Ramanathapuram, Madurai and Manamadurai in Tamilnadu State, India. The firing temperature of bricks were estimated by refiring the samples to four different temperatures from 600 to 900°C in steps of 100°C in air in an electric muffle furnace for 2 h and recording the corresponding FTIR spectrum. Firing conditions of bricks were inferred from the observation of appearance or disappearance of octahedral sheet structure of silicate and the characteristic absorption positions of the bands due to the presence of iron oxides. The results showed that bricks from Ramanathapuram, Madurai and Manamadurai were fired to a temperature of above 900, around 800 and 700°C respectively. In addition, room temperature Mossbauer measurements were carried out to confirm FTIR results. The development of strength and reduction in porosity of the above bricks were noticed at elevated temperatures due to enhanced vitrification.

INTRODUCTION

The term clay is commonly used in the earth sciences to designate natural mineral assemblages that consist predominantly of fine-grained material. In these, a large proportion of minerals has particle sizes that lie in the clay fraction (< 2μm) (Murad and Wagner, 1989). The main constituents of clay are Si, Al and water, which also contains small amounts of feldspars, carbonates, Fe, Ti, Mg, Mn and K oxides, as well as soluble salts and organic matter.

Clays are the classic raw materials for the production of bricks. Learning to transform clay into brick by firing is an important step. For brick manufacturing, clay must possess some specific properties and characteristics. Such clay must have plasticity, which permits them to be shaped or molded when mixed with water; they must have sufficient wet and air-dried strength to maintain their shape after forming. Also, when subjected to appropriate temperatures, the clay particles must fuse together. There are three ways to form the shape and size of a brick: extruded, molded and dry pressed. The majority of brick are made by the extrusion method. In India, brick making is typically a manual process i.e., extrusion method. There are about 400 brick industries, located in Ramanathapuram, Madurai and Manamadurai regions employing around 4000 people. Most of these industries are rural based. These industries are the major contributors towards housing in rural as well as urban areas. Therefore, the evaluation of quality of these bricks is an important one because brick from the same manufacture will have slightly different properties in subsequent production runs but brick from different manufacturers that have the same appearance may differ in other properties. Clay bodies undergo several changes during drying and firing stages as a result of physical, chemical and mineralogical modifications. In structural clay products, these changes are essentially brought in to enhance mechanical strength and durability properties (Brownell, 1976). The quality of bricks are deduced from the magnitude of thermal changes, which largely depend on the mechanical and mineralogical make up of clay mass, besides temperature of exposure and its duration, fabric of clay mass and interparticle separations.

Thermal transformations in clay based materials during firing provide a means to estimate their firing temperature. Dhanapandian *et al.*,2009 and Manoharan *et al.*, 2008 have successfully used FTIR and Mossbauer spectroscopic techniques on clay-based materials in order to determine their firing temperature and firing condition.

Hence FTIR and Mossbauer are the two techniques employed in the present work to estimate the firing temperatures achieved by brick making people in the brick industry and firing techniques adopted for the bricks collected from the three different regions of Tamilnadu,

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Table 1. Estimated firing temperature of industrial clay bricks collected from Ramanathapuram (RPM), Madurai (MDI) and Manamadurai (MMDI)

Sample ID	Nature of material	Colour	Atmosphere prevailed	Dehydroxylation of hydroxyl band	Expandable layer silicates	Estimated firing temperature
RPM	Clay brick	Red	Oxidizing	Completed	Destructed	> 900°C
MDI	Clay brick	Red	Oxidizing	Completed	Destructed	~ 800°C
MMDI	Clay brick	Red	Oxidizing	Completed	Destructed	~ 700°C

Table 2. Room temperature Mossbauer parameters

S.No.	Sample location	Nature of material	Colour	Sample ID		I.S. (mm/s)	Q.S (mm/s)	H (kOe)	I_{rel} (%)	Assignment	Estimated firing temperature	Estimated firing atmosphere
1	Ramanathapuram	Clay brick	Red	RPM	S	0.37	-0.20	512	47.17	Hematite	> 900°C	Oxidizing
					D_1	0.42	0.81	---	49.56	Fe^{3+}		
					D_2	1.10	2.34	---	3.27	Fe^{2+}		
2	Madurai	Clay brick	Red	MDI	S	0.38	-0.22	499	35.73	Hematite	~ 800°C	Oxidizing
					D_1	0.41	0.99	---	55.88	Fe^{3+}		
					D_2	1.14	2.32	---	8.39	Fe^{2+}		
3	Manamadurai	Clay brick	Red	MMDI	S	0.38	-0.21	497	14.05	Hematite	~ 700°C	Oxidizing
					D_1	0.45	1.31	---	68.68	Fe^{3+}		
					D_2	1.16	2.31	---	17.27	Fe^{2+}		

I.S. – Isomer shift; Q.S. – Quadrupole splitting; H – Magnetic hyperfine field; I_{rel} – Relative percentage area

India. An attempt have also been made to study the quality of bricks by submitting to technological tests.

MATERIALS AND METHODS

For the present investigations, industrial clay bricks from three different regions of Tamilnadu State namely Ramanathapuram (RPM), Madurai (MDI), Manamadurai (MMDI) (Fig.1) were selected and subjected to FTIR, Mossbauer and mechanical analysis.

Fourier Transform Infrared Spectroscopy (FTIR)

Industrial brick samples were refired in air in an electric furnace at temperatures ranging from 600 to 900°C in steps of 100°C increment. The samples were kept in respective temperature for two hours and allowed to cool in the furnace to room temperature. The FTIR absorption spectra were recorded in the explored range of frequencies 4000-400 cm^{-1} for the refired samples using Model 330 Nicolet Avator FTIR spectrophotometer. The samples were Pelletized by mixing with the spectra grade kBr at the ratio of 1:20 by weight. The kBr pellet of 13 mm diameter was kept inside the sample holder and scanned at 1 cm^{-1} resolution. Each time before recording the spectra of samples the instrument was calibrated using polystyrene film as standard.

Mossbauer and mechanical measurements

^{57}Fe Mossbauer spectra were recorded at room temperature (RT) in transmission mode with a conventional constant acceleration spectrometer equipped with a ^{57}Co (Rh) source. Absorbers were prepared from powdered sample with a thickness of 100 ± 10 mg/cm^2 using a PMM compression holder. The spectra were computer-fitted to a sum of Lorentzian lines by applying the constraints of equal line width and areas in the ratio 3:2:1:2:3 for the six peaks of sextets. Isomer shifts were referred to the centroid of the spectrum of α-Fe at RT. The relative concentration of the different Fe species was calculated from the spectral area ratio assuming that the factor (probability of Mossbauer effect) is the same in all the implicated species.

The compressive strength of the industrial bricks is determined by dividing the maximum load with the applied load area of the bricks. The flexural rupture strength of the bricks is determined by three points bending test of a constant cross-head speed of 0.5 mm/min. Water absorption and porosity of the respective industrial bricks were determined by using the Archimedes water displacement method. Bulk density was measured dividing the mass by the external volume for each sample.

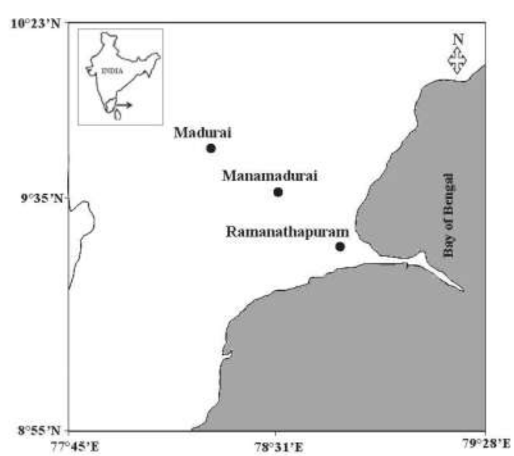


Fig. 1 : Location Map of clay bricks investigated [Ramanathapuram (RPM), Madurai (MDI) and Manamadurai (MMDI)]

RESULTS AND DISCUSSION

Figs. 2-4 represent the room temperature FTIR absorption spectra of brick samples. From the FTIR spectra of the brick samples the lower limit of firing temperatures were estimated (Table 1). According to Bantignies *et al.,*1997,

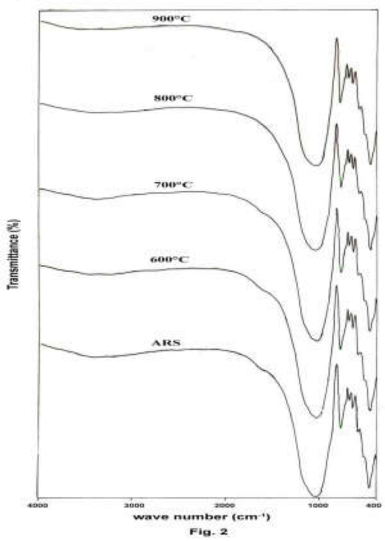


Fig. 2 : Room temperature FTIR absorption spectra of brick samples from RPM in the as received state and at different refiring temperatures

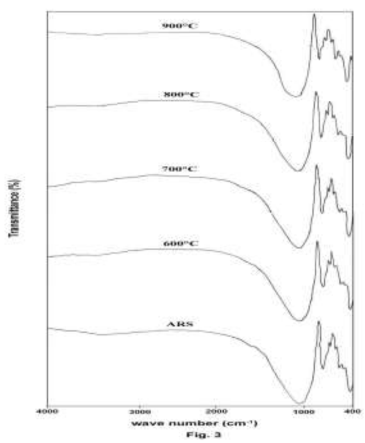


Fig. 3 : Room temperature FTIR absorption spectra of brick samples from MDI in the as received state and at different refiring temperatures

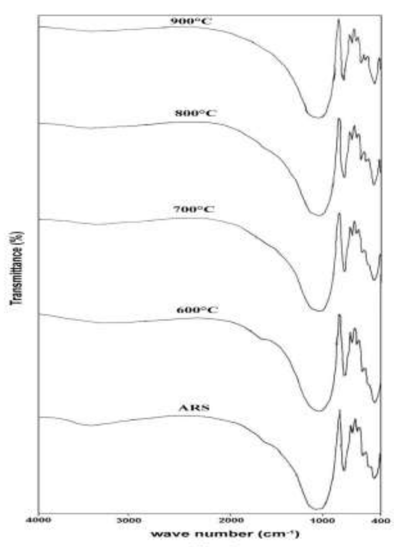
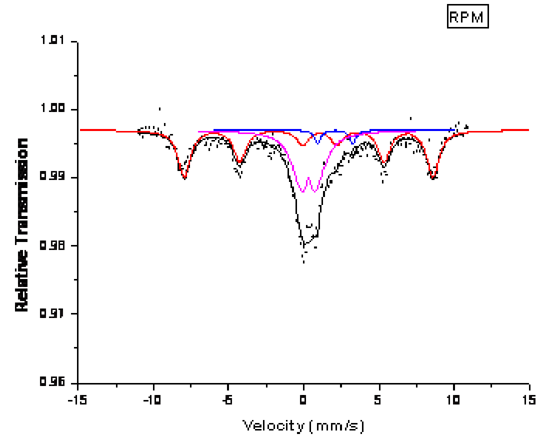
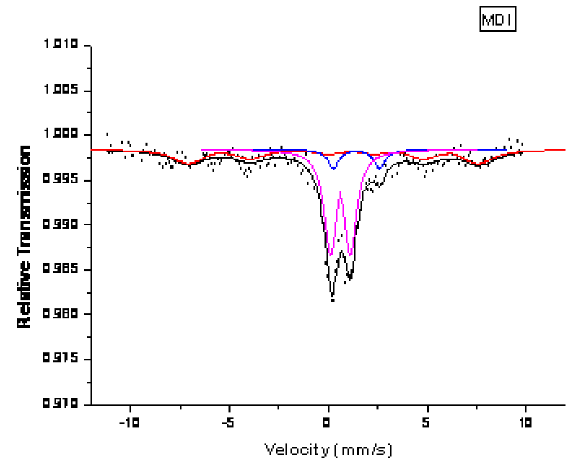


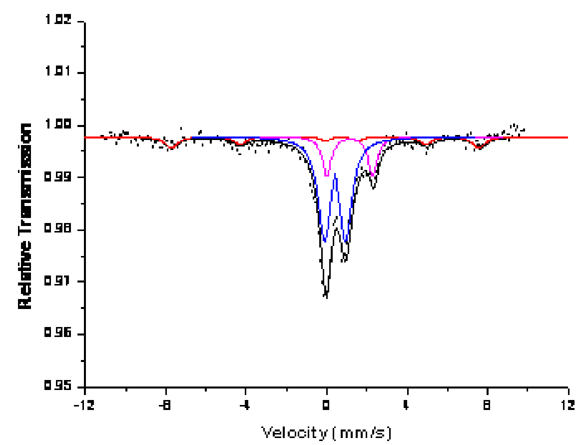
Fig. 4 : Room temperature FTIR absorption spectra of brick samples from MMDI in the as received state and at different refiring temperatures



(a)



(b)



(c)

Fig. 5 : Room temperature Mossbauer spectrum of industrial claybricks from (a) RPM (b) MDI (c) MMDI

the characteristic infrared absorption bands around 3700, 3670, 3655 and 3622 cm^{-1} are due to O-H stretching region of kaolinite in ordered form, whereas the disordered form of kaolinite can be characterized by the presence of the bands around 3700 and

3622 cm^{-1} (Bantignies *et al.,*1997; Ramaswamy and Venkatachalapathy,1992). Wagner *et al.,*1999 have reported that kaolinite dehydroxylates at about 400-450°C during heating in air. The absence of the above absorption bands for the brick samples from RPM, MDI and MMDI indicates that they were fired to temperature of above 450°C. The O-H deformation vibrational modes are separated into two bands at 940 and 918 cm^{-1} which arise from intersheet and intrasheet hydroxyls which begin to disappear with increasing temperature (Bantignies *et al.,*1995). Elsass and Oliver (1978) reported that at 500°C the above bands are completely absent. None of the brick samples taken for the present study showed the band at 940 and 918cm^{-1} implying that all samples were fired above 500°C.

Around 600°C the expandable layer silicates collapse, resulting a broad symmetry band centered around 1030 cm^{-1} or 1080 cm^{-1} for red and white type clay respectively (Wagner *et al.,*1999; Ghosh, 1978). In the present work, one was observed a strong symmetry band at around 1030 cm^{-1} for all brick samples implying that red type clay out of which brick materials were made and destruction of silicate structure.

In order to determine the maximum original firing temperature of clay bricks, refiring methodology can be followed in which no changes in the FTIR spectra are to be expected during laboratory refiring of bricks until the refiring temperature exceeds the original firing temperature (Wagner *et al.,*1998). FTIR absorption spectrum of RPM in the as received state is similar as one obtained at 600, 700, 800 and 900°C. FTIR spectrum of MDI in the as received state is similar up to 800°C but at 900°C the intensity of the band 580 cm^{-1} is increased, whereas in the case of MMDI the changes were observed at 800°C and 900°C (see band intensity of 580 cm^{-1}). This implies that brick samples collected from RPM, MDI and MMDI were fired to a temperature above 900°C around 800 and 700°C during its manufacturing in the industry respectively.

The absorption bands at 580 and 540 cm^{-1} are attributed to iron oxides (Barilaro *et al.,*2005; Russel and Wilson, 1987). The presence of iron, either in pure state or in the form of oxides is the key factor to understand the colour of the bricks. The colour of the brick is due to the content of iron oxides which acts as the colouring agent. Acchar et al. (2006) have reported that the presence of significant amount of iron oxide (Fe_2O_3) is responsible for a reddish colouring of the clay based materials after firing in an oxidizing atomosphere. The red colour of the brick samples shows the presence of hematite. The presence of hematite reveals that the samples were fired under oxidizing atmosphere or due to the air allowed into the kiln at the time of firing. The absorption bands at 775 coupled with 695 cm^{-1} are attributed to the presence of quartz (Ojima, 2003). In the present work, quartz was identified as predominant and makes the clay self-tempered during heating.

^{57}Fe room temperature Mossbauer spectrum of RPM industrial clay brick (fired) in the as received state (Fig. 5a) show mainly a paramagnetic doublet in the central part of the spectrum attributed to Fe^{3+} species and a magnetic six-line pattern with a hyperfine field value of 512 kOe is attributed to α-Fe_2O_3 (magnetically ordered and well crystallized hematite due to high firing temperature). Mossbauer spectra of both MDI and MMDI (Figs. 5 b,c) show the typical pattern of mainly a paramagnetic doublet in the central part of the spectrum along with the percentage area of magnetic component as 35.73 and 14.05 respectively (Table 2). Mossbauer spectra of both MDI and MMDI also exhibit the presence of a characteristic weak second doublet attributed to Fe^{2+} species having percentage area of 8.39 and 17.27 respectively. The iron in clays may be present as structural Fe^{2+} or Fe^{3+} in the silicate structures of the clay materials, in other silicates and in particles of iron oxides or oxyhydroxides adhering to the clay mineral particles. Well-crystallized iron oxides show the characteristic six line pattern arising from the magnetic hyperfine interaction (Wagner *et al.,*1992). According to Murad and Wagner (1989) following dehydroxylation of clay minerals, the quadrupole splitting of octahedrally co-ordinated Fe^{3+} species increases abruptly, but reverts to lower values upon the formation of new, better ordered phases at high temperatures. According to Wagner et al. (1992), when firing the clay minerals around 750°C it is possible to get 30% of the iron as hematite, will show a six-line pattern at room temperature. As can be seen, the presence of high content of Fe^{3+} species in the spectra of RPM, MDI and MMDI brick samples indicating that brick samples were fired in an oxidizing atmosphere. Quadrupole splitting values of doublet [Fe^{3+}] obtained in the present work allow one also to infer a rough estimation of the firing temperatures as above 900 and around 800 and 700°C for samples RPM, MDI and MMDI respectively. The Mossbauer results are in agreement with FTIR results.

The physical properties such as compression strength, flexural rupture strength, water absorption, porosity and bulk density of the industrial bricks collected from RPM, MDI and MMDI were measured. The compressing and flexural rupture strength tests are the most important tests of assuring the engineering quality of a building material (Weng *et al.,*2003). Both compressive strength and absorption are affected by properties for clay, method of manufacture and degree of firing. For a given clay and method of manufacture, higher compressive strength values and lower absorption values are associated with higher firing temperatures. The results indicate that the strengths are greatly dependent on the firing temperature. The compressive strength of brick samples collected from RPM, MDI and MMDI in the as received state were measured as 7.28, 6.75 and 5.32 MPa, where as the flexural rupture strength of the above samples were measured as 3.34, 2.85 and 2.13 MPa respectively.

Water absorption is a key factor affecting the durability of brick. The less water infiltrates into brick, the more durability of the brick and resistance to the natural environment are expected. Thus, the internal structure of the brick must be intensive enough to avoid the intrusion of water. The water absorption rate is also been used as an indication for porosity of the brick. If cavities or porosity are more in the matrix, specimens will exhibit less density and absorb more water. During sintering open and closed pores are usually formed. The minimum density corresponds to the maximum volume of closed pores in the specimens. Densification is a pore-filling process that occurs during the liquid phase flow and by pore shrinkage (Lin, 2006). The water absorption, porosity and bulk density of the above samples in the as received state have also been measured as 12.53, 14.48, 18.10%, 15.45, 18.71, 20.36% and 1.86, 1.75 and 1.62 gm/cm^3 respectively. It is important to note that on refiring the brick sample MDI to 900°C, the water absorption and porosity values decreases to 13.01 and 16.32%, respectively. Bulk density value of the above sample increases to 1.81 gm/cm^3. In the case of MMDI, on refiring to 800 and 900°C, the water absorption value decreases to 16.72, 13.40% and porosity value decreases to 19.58, 17.33%, respectively. Bulk density of the sample is found to be 1.67 and 1.77 gm/cm^3.

Conclusion

This work has demonstrated to produce an engineering quality of industrial clay bricks. In this work it is found that the firing temperature is a key factor to enhance the quality of bricks. Bricks collected from RPM exhibited better mechanical properties than that of MDI and MMDI. The quality of bricks from MDI and MMDI can be further improved by firing to the temperature 900°C during its manufacturing in the industry.

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