

Compositional and Technological Features of Fired Brick Samples Excavated from Gangaikondacholapuram, Tamilnadu (India)

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ARTICLE INFO

Article history:

Received: 24 November 2015;

Received in revised form:

8 April 2016;

Accepted: 12 April 2016;

Keywords

FT-IR,
XRD,
SEM/EDS,
Firing Techniques,
Ancient Brick Samples.

ABSTRACT

With the aim of contributing to the knowledge of South-India Medieval age brick production, the mineralogy of briquettes excavated from the site of Gangaikondacholapuram (India) has been studied in order to make inferences concerning the clay preparation and firing techniques of that period. In this work, the fired brick finds (GKSB-1 to GKSB-5) were analysed by three distinct techniques namely Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and SEM/EDS to determine their mineralogical, chemical compositions and microstructures respectively. The relative similarity of compositions, the fine, dense and homogeneous microstructures and the presence of high-temperature phases such as pyroxenes, mullite, analcime and wusite in the sample coded GKSB-1, GKSB-3 and GKSB-5 showed the use of high firing temperatures, in the range 900–1000°C. While the presence of kaolinite and halloysite clay minerals in the briquettes GKSB-2 and GKSB-4 suggests the low temperature of firing ($\approx 600^\circ\text{C}$) and may be related to adobe bricks, all indicate the adoption of non-calcareous clay with specialized brick making techniques by the brick makers of Gangaikondacholapuram in the 11th to 12th millennia CE.

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Introduction

Archaeology is the scientific study of the past through material remains that are left behind by human activities. Based on the analysis of these remains, we try to reconstruct the daily lives and customs of past societies and offer possible explanations for changes in societies and cultures over time. The visible remnants of human occupation, in general, of buildings, burial places, implements, utensils, and ornaments belonging to periods about which there are no written records. The excavation at this archaeological site may reveal the depth of civilization. Also, the unearthed clayware, broken statues, ceramic shreds, corroded armor, weapons, etc., give valuable information about the material environment during the ancient times [1,2].

Of various archaeological ceramic artifacts, bricks are the most popular ceramic building materials of human societies from the first villages settled before the invention of pottery to many modern towns and cities, which kept people warm in the winter and cool in the summer for thousands of years. Thousands of archives have been discovered, but an enormous amount of material has been lost. Only a fraction of available archaeological sites have been surveyed, and only a fraction of surveyed sites have been excavated. Hence, it is important to understand that remain as the primary source of authority [3].

Hence the present work is aimed at the characterization of brick samples excavated from Gangaikondacholapuram (GKS) archaeological site of Tamilnadu by a combination of Fourier transform infrared (FTIR) spectroscopy, powder X-ray diffraction (PXRD) and scanning electron microscopy

(SEM-EDS) to give a detailed picture of the mineralogical assemblages, degree of vitrification and elemental composition. An attempt was made to define the firing process that leads to the information about the firing temperature achieved and the firing conditions maintained in the firing kiln by the artisans at the time of manufacture.

Experimental procedure

Sample and site details

Gangaikondacholapuram is located in Jayangondam Taluk of Perambalur District. Excavation conducted at two locations at Maligaimedu revealed the remains of royal palace, built with burnt bricks. The ceilings covered with flat was fortified with laterite fort wall which throwing light on the link between the Chola dynasty and South-East Asia, during the period from the 10th century to 13th century. The thickness and height of the fortified wall measured 2.15 m and 1.35 m respectively. The archaeological brick samples selected at different depths of the trench are coded as GKSB-1, GKSB-2, GKSB-3, GKSB-4 and GKSB-5. After removal of surface layers, the remnants of interest are prepared for the analysis. The photograph of representative samples is shown in Fig. 1.

FT-IR studies

The infrared spectra were recorded in the mid IR region 4000–400 cm^{-1} using Perkin Elmer FTIR interferometer by KBr pressed pellet technique by mixing the powdered samples with KBr in weight proportion of 1:20. The precision of the FTIR instrument is 4 cm^{-1} .

XRD studies

In order to identify the crystalline phases present in the

specimens, the samples were subjected to XRD analysis (XPRT-PRO diffractometer). The studies were carried out using CuK α radiation in the 2θ range of 3–80°.

Microstructural studies

After polishing, the samples were coated with a thin film of gold and subjected to SEM examination (JSM-5610 scanning electron microscope). The phase compositions of certain zones in the microstructures were determined by an energy-dispersive X-ray analyser (EDX) attached to the SEM.



Fig 1. Archaeological brick samples from GKS site

Results and Discussion

Fourier Transform Infrared Spectroscopy

The FTIR spectra of representative architectural brick fragments are shown in Fig. 2. The estimation of firing temperature and the atmosphere condition prevailed during manufacture is portrayed in Table 1.

From the FT-IR spectra of GKS-2, it is revealed that the four hydroxyl bands appeared at wave number 3690, 3675, 3649 and 3620 cm^{-1} and Si-O stretching band centered at 1036 cm^{-1} with the asymmetry at 914 cm^{-1} attributed to Al-OH vibration are typical of kaolinite. These bands are sensitive to temperature effects. Thus, the existence of both hydroxyl and Al-OH vibration band in the received state is an evidence for that GKS-2 must be heated to a temperature less than 500°C during manufacturing as these bands are sensitive only up to 500°C [4,5].

Adobe is an ancient form of brick consists of earth (mud, silt and sand) and water. Occasionally, straw is also present in the structure to enhance mechanical resistance. Adobe does not go through a firing process; instead, it is submitted to a prolonged period of drying, usually carried out by exposing the material to the sunlight. An adobe building can last hundreds of years and it is totally recyclable. Hence we may conclude that, GKS-2 coded brick really heated very low temperature or it falls under the category of adobe bricks [6].

The dehydroxylation of kaolinite mineral takes place at temperatures 500°C and 600°C. The reaction is getting completion by about 750°C or 800°C. Hence the presence of hydroxyl bands at 3621 cm^{-1} in the received state IR spectra of GKS-4 suggests that the firing temperature achieved was below 800°C and denotes incomplete dehydroxylation.

While its absence in GKS-1, GKS-3 and GKS-5 sample represents the completion of dehydroxylation and hence may be fired above 800°C. This dehydroxylation is followed by the crystalline frame work collapse, destruction of octahedral sheet structure and hence broadening of the Si-O stretching band in the 1100-1000 cm^{-1} with firing temperature [7].

Shoval and Beck [8] have stated that the position of prominent infrared absorption band due to Si-O stretching mode is influenced by the firing temperature of the brick and hence relevant to estimate the firing temperature range. To be precise two different absorptions of wave number about 1030 cm^{-1} and 1082 cm^{-1} caused by silicate band indicate that the firing temperature ranges achieved would be 700°C and 900°C respectively.

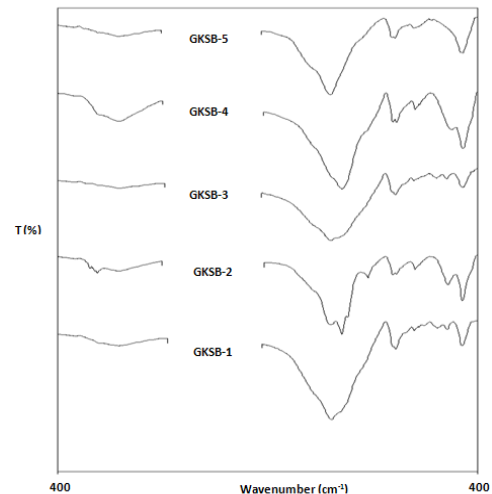


Fig 2. FT-IR spectra of GKS brick samples

For the briquettes GKS-1, GKS-3 and GKS-5, the Si-O stretching band positioned around 1080 cm^{-1} reveals that the firing temperature reached during brick manufacturing may be fall at 900°C or above. Accordingly, the silicate bands situated in the wave number at 1036 cm^{-1} and 1035 cm^{-1} for GKS-2 and GKS-4 respectively shows that the temperature at which the brick is fired will lie in the range 700-800°C [9].

The presence of iron oxides in the region of 700-400 cm^{-1} formed during the firing process of clay is due to the replacement of aluminium by iron. Some iron oxides that do not normally occur in natural clays may form during firing of artifact. Magnetite may form during firing under reducing condition and hematite during oxidizing condition [10,11].

Each and every Gangaikondacholapuram brick relic (except GKS-3) simply displayed the infrared absorption band due to hematite (583 cm^{-1}). This result clearly shows that these samples were fired under oxidizing atmosphere. Conversely the occurrence of magnetite (583 cm^{-1}) in GKS-3 suggests that it might have been fired in reducing atmosphere or in the closed kiln with proper air supply into the kiln. Thus, the craftsman of Gangaikondacholapuram site was aware of both the oxidizing and reducing atmosphere condition of the manufacturing process.

X-ray diffraction analysis

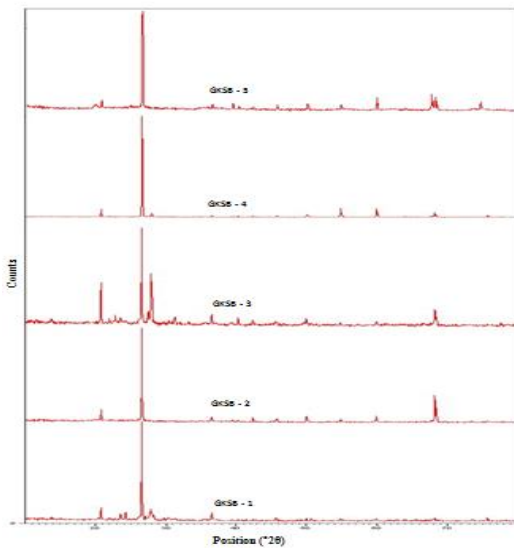
The XRD patterns taken on the specimens of ancient bricks excavated from Gangaikondacholapuram are presented in Fig. 3. The patterns thus obtained are compared with standard dataset of the Joint Committee for Powder Diffraction Standards (JCPDS), for the identification of crystalline mineral phases [12].

In the present study, GKS-1 relic have the X-ray peaks of quartz ($d = 4.27, 3.35$ and 1.80 \AA), plagioclase – albite ($d = 3.20 \text{ \AA}$), K-feldspar (orthoclase) ($d = 3.77, 1.98$ and 1.28 \AA) and hematite ($d = 2.51 \text{ \AA}$) with its strong d -spacing values. Besides that the high temperature firing minerals of pyroxene ($d = 3.15 \text{ \AA}$), chrysotile ($d = 3.66$ and 2.46 \AA) and analcime ($d = 3.42$ and 2.93 \AA) were also be found.

On the contrary, the ceramic brick fragment GKS-2 is characterized by the clay minerals halloysite (7.53 \AA) and kaolinite (1.98 and 1.67 \AA), quartz ($4.26, 3.35$ and 1.82 \AA) and hematite (2.69 \AA) with its strong basal reflection. Whereas the sample GKS-3 indicates the existence of quartz ($d = 4.27, 3.35$ and 1.82 \AA), feldspar mineral albite ($d = 4.04$ and 3.19 \AA) and orthoclase ($d = 3.77$ and 3.23 \AA) as the major constituents.

Table 1. Estimated firing temperature and prevailed atmosphere condition of Gangaikondacholapuram brick fragments

Brick code	Dehydroxylation of hydroxyl band	Octahedral sheet structure	Position of the silicate band (cm ⁻¹)	Estimated firing temperature (°C)	Existence of iron compounds	Firing atmosphere prevailed
GKSB-1	Completed	disappeared	1081	> 800	Hematite	oxidizing
GKSB-2	Incomplete	appeared	1036	< 500	Hematite	oxidizing
GKSB-3	Completed	disappeared	1081	> 800	Magnetite	reducing
GKSB-4	Incomplete	disappeared	1035	<800	Hematite	oxidizing
GKSB-5	Completed	disappeared	1083	>800	Hematite	oxidizing

**Fig 3. X-ray diffraction pattern of GKS bricks**

Moreover the crystalline phases of olivine, pyroxene and the iron oxide minerals like wustite ($d = 2.13 \text{ \AA}$) and magnetite ($d = 2.98 \text{ \AA}$) are also be identified. Considering the examined briquettes GKSB-4 and GKSB-5, both of them exhibits the crystalline mineral phases of quartz, feldspar (albite) and hematite as common. Apart from that, the relic coded GKSB-4 contains the phyllosilicate mineral muscovite additionally as evidenced by the reflection at $d = 1.99 \text{ \AA}$.

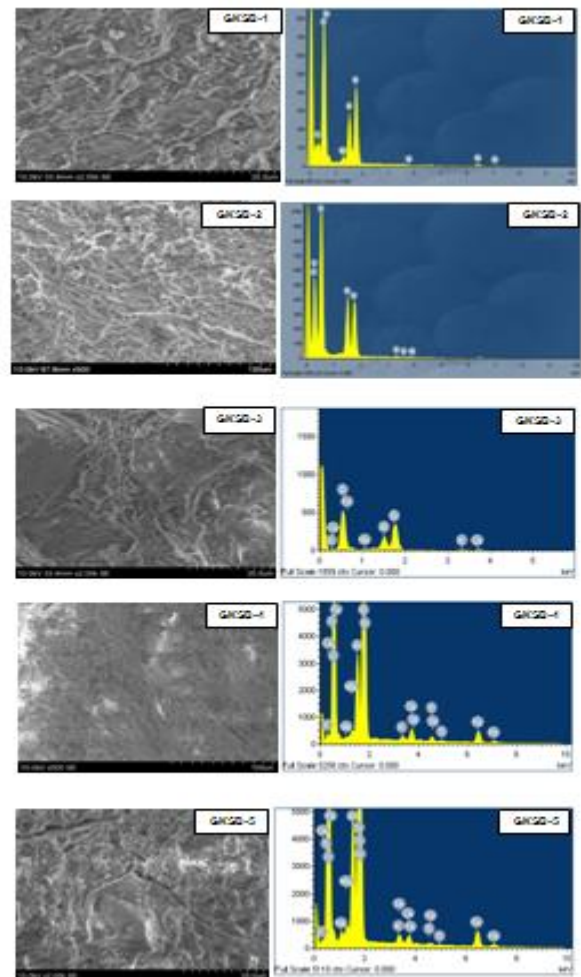
Scanning Electron Microscopy with Energy Dispersive Spectroscopy

The SEM microstructure and EDS spectra of GKS brick fragments are given in Fig.4. The type of the clay used, firing conditions achieved by ancient artisans at the time of brick making are depicted in Table 2. The concentration of elements and their values is tabularized in Table 3. The wt% of CaO of all briquettes is < 6% and hence it belongs to non-calcareous (NC) nature [13].

Degree of Vitrification

The morphology of GKSB-1 shows a continuous vitrification stage and a wide area of glassy phase that indicating the firing temperature of about 1050°C [14,15]. While the SEM image of GKSB-3 and GKSB-5 establishes the continuous vitrification stage (CV) associated with a fine bloating pores.

Here the microstructure pattern and the behavior of these samples is similar to the one described by Maniatis and Tite [13] and Xiaohui Chenget al [16] for the archaeological relics. The clay was in continuous vitrification stage of non-calcareous type may be fired in the temperature range 900-1000°C for GKSB-5 in the oxidizing atmosphere while 850-950°C for GKSB-3 under reduction condition.

**Fig 4. SEM photomicrographs and EDS spectra of GKS briquettes**

The fragment GKSB-2 and GKSB-4 shows no vitrification microstructure. The micrograph of this sample shows a flat surface containing spherically shaped pores. The voids and cracks of various arbitrary shapes are also seen. This allowed us to interpret that these bricks from GKS was fired at relatively low temperatures (800°C) in the oxidizing condition [13,17].

Elemental composition

EDS analysis results show that the bricks contain high amounts of oxygen (O), silicon (Si), aluminium (Al) and Iron (Fe), low amounts of sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca) and traces of Sr, Te, Tl and Cl. The presence of low amounts of Ca in their composition supports the notion of the use of calcium poor clays from raw material sources.

Table 2. Vitrification stages and firing temperature ranges of GKS brick samples

Sherd code	% CaO	Clay type	Vitrification stage	Firing temperature (°C) (atmosphere)
GKSB-1	0.76	NC	CV	900 – 1000 (O)
GKSB-2	0.53	NC	NV	< 800 (O)
GKSB-3	2.86	NC	CV(fb)	850 – 950 (R)
GKSB-4	2.89	NC	NV	< 800 (O)
GKSB-5	1.44	NC	CV(fb)	900 – 1000 (O)

Table 3. Elemental composition of the (GKS) bricks

Elements	Elemental composition – weight percents (%)				
	GKSB-1	GKSB-2	GKSB-3	GKSB-4	GKSB-5
O	54.43	52.15	51.02	52.40	53.56
Si	22.64	23.20	22.54	23.84	24.25
Al	15.06	16.13	9.35	8.50	8.73
Fe	5.43	6.27	12.70	7.06	6.41
Ca	0.54	0.38	2.05	2.07	1.03
Mg	0.86	-	-	1.03	1.28
K	-	0.45	1.67	0.69	1.00
Na	-	-	0.67	0.48	1.07
Ti	-	-	-	1.35	0.39
C	1.04	1.42	-	-	-
Sr	-	-	-	1.92	1.84
Te	-	-	-	0.66	0.44

The element oxygen and silicon shows the quartz (SiO_2), while feldspar exhibits the lines of Ca, Na, Al, and K. The kaolinite clay matrix contains much aluminium, silicon and oxygen. The presence of Fe recorded with EDS corresponds with XRD results showing that hematite (Fe_2O_3) or magnetite (Fe_3O_4) mineral. The carbon element refers the organic material that is accidentally included due to its environmental conditions or deliberately added to the clay by brick makers to improve its plasticity [16,18]. The trace elements may be due to impurities and/or foreign inclusions.

Conclusion

The Gangaikondacholapuram archaeological brick finds were scientifically analysed by FT-IR, XRD and SEM-EDS to infer the knowledge about raw materials and firing technology of our ancestors. The final results of the studies revealed that the people lived at the time of manufacture of these ceramic products in the respective areas of the excavation were aware of two types of atmosphere condition i.e. the perfectly oxidizing and reducing conditions achieve good quality of their products. Moreover, the Gangaikondacholapuram brick makers have the ability of making adobe bricks. It is sun dried bricks with good mechanical strength and environmental friendly. Thus the artisans at this site are very conscious about their surroundings and technology.

Acknowledgment

The authors are thankful to the Superintending Archaeologist, Archaeological Survey of India, Chennai (ASI) for providing archaeological brick samples for this work. The authors are grateful to the Staff-in-charge, Centralized Instrumentation Service Laboratory (CISL), Annamalai University, Annamalainagar for giving permission to complete FT-IR studies. Thanks to Dr. C. Sanjeeviraja, Professor and Head, Department of Physics, Alagappa University, Karaikudi for taking XRD studies. The author acknowledges S. Prathap Augustine, Hyderabad for SEM-EDS microanalysis.

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