Asian Building Techniques for Colonial Manila: Reviewing the Concept of Cultural Hybridity

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Research article

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Abstract

Historical building techniques have been pointed out as a sample of local resistance to colonial technical influence during the early modern period, although this could not be proven by chemical analysis. A clay brick with an attached lime mortar sample was acquired from the former San Francisco Church's foundation in Intramuros, Manila, Philippines and representative portions (BRK-1, BRK-2, BRK-3, MTR-1, MTR-2, and MTR-3) of the sample were utilized for chemical analysis using various analytical techniques. These are the energy dispersive x-ray fluorescence (EDXRF), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and ultraviolet-visible spectroscopy (UV-Vis) for quantifying organic compounds. The clay brick sample is made of typical sand and clay specifically composed of non-calcareous clay and low refractory fluxes. The brick's firing temperature was determined to be between 600°C to 800°C in an oxidizing environment. The attached lime mortar sample is probably manufactured using crushed seashells and classified as a hydraulic lime where clayey and sand particles serving as pozzolans. The lime mortar's microstructure shows that it is well carbonated. Possible organic compounds specifically egg whites (albumen) which may have been added to the lime mortar yielded negative results. Both qualitative tests (Xanthoproteic Test, Ninhydrin Test and Biuret Test) and quantitative assays (Biuret Assay and Bradford Assay) were not able to detect the presence of any proteinaceous compounds in the sample. It has been established based on this material sample that eighteenth century Asian builders working in Manila kept local traditions and rejected European preferences.

Introduction

Analysing cultural heritage from a physico-chemical and biological perspective has opened a wide range of possibilities in the last decades [1]. Not only does it provide a fruitful scientific approach to conservation and restoration, but it also contributes immensely to historical perspectives. In line with this, previous studies on early modern art and architecture have underlined the importance of redefining the concept of cultural hybrid [2, 3]. Considering Latin American and Asian heritage as a progressive adaptation of European aesthetic qualities, current studies are reinforcing the local role and the effects of cultural and technical resistance. Apart from taste issues, artistic and specially building techniques have been pointed out as crucial contributions by colonial artisans from a hypothetical perspective [4]. Archival materials are usually elusive with regards to these information and chemical analysis is not normally being done. Therefore, some oral traditions about the use of several materials such as eggs, sugar, blood or milk, persist. Material remains are also affected by natural disasters, renovations, speculations or even non-professional restorations, hence, acquiring historical samples tend to be difficult [5].

Philippine architecture is a good starting point of this approach for several reasons. First, its historical development combines Asian, American and European techniques, a phenomenon emphasized by the lack of Spanish workers. Recent research about Chinese techniques provided a required base for such cross-case analysis [6]. Despite this, its heritage has been usually considered as a colonial imposition, or Chinese influence, with little local contribution, while recent studies are underlining the contrary. Second,
some historical sources are exceptionally detailed about building materials, although this information has not been verified with chemical analysis. Third, recent archaeological findings in Intramuros, Manila facilitated the acquisition of building materials from eighteenth century remains, not affected by recent interventions.

In this context, this paper aims to demonstrate that eighteenth century builders in Manila kept local techniques when working for colonial institutions. To achieve this, historical sources on building processes in Manila at that time were compared with Chinese and European influences was included in this study. Then, some archaeological remains from the original San Francisco convent in Intramuros, Manila was integrated in the discussion. Chemical analysis was used to determine the provenance and techniques employed by the local artisans in manufacturing the brick and mortar materials. The microstructure and chemical components of the samples were analyzed with the combination of energy dispersive x-ray fluorescence (EDXRF), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscope (SEM). Possible organic compounds added to lime mortars was also investigated.

Choosing between three cultures: Building techniques in eighteenth century Manila from historical sources.

Different historical documents point out that building in colonial Manila was a mixture from at least three different traditions: local, European and Chinese. This blend can be found from Tagalog dictionaries published at that time [7]. Leaving aside the rich terminology on carpentry, other building terms are included, such as brick (ladrillo), mortar (argamasa), stone (bató), lime (apog), cut stone (batlag) or paste ashlers with mortar (hacab). The first two terms are clear linguistic loans from Spanish. At the same time, none of these cases can be considered of Chinese origin. Then, the rest were vernacular before the European contacts. Other terms used for units of measurement were included in the local languages such as caban for lime (about 55,5 l.) and carga for sand (222 l.), the former is a vernacular term, while the latter is a loan from Spanish.

Philological approach can be enriched from data included in eighteenth-century building contracts preserved in archives. One of the most detailed documents on techniques is that of Tondo church, built in 1727 were bricks and stone were used in walls by its Chinese builders [8]. From its documents it can be said that the most common ashlers in Manila were the sillar de a cinco (ca. 100 × 50 × 25 cm.) and the sillar ordinario (83,5 × 42 × 21 cm.), being displayed with brick rows. Similar solutions are found in contemporary buildings in Manila and neighbouring provinces. A first example is Santa Potenciana cistern (1762), where the Chinese Juan Peauco followed a similar display, including duck eggs and sugar cane honey in the mortar as a waterproof solution [9]. Some of these elements were analysed from chemical perspective in recent studies [10, 11, 12]. A slightly later work was the cistern for San Francisco convent, by Vicente Laureano de Mémije (1778), whose project informs about the materials in details, including 150 ashlers, 80.000 bricks, 3.000 quadrangular bricks, 888.000 l. of lime (16.000 cavanes) and 3.552.000 l. of sand (16.000 cargas), apart from other vegetal materials that were just cited in the general budget. Such quantities would coincide with the later description of Philippine mortars by Herbella:
“Generalmente se suelen mezclar de dos y media a tres partes de arena, en volumen, por una de cal” (Usually, from two and a half to three parts of sand, in volume, for one of lime, are blended) [13]. Contemporary to Herbella, Valdes registered several solutions in the Philippines and China which were probably active in the eighteenth century. For walls 1 of oyster lime corresponded to 2 of sand and 0.5 of rice straw or 1 of maladquit mud. This mud may be referring to the historical spelling of Malaguit river or probably river mud in general. The use of rice straw should be understood as a way of improving adhesiveness of mortar. For roofs, 3 of lime matched with 2 of rice straw, while 1.5 of brown paper was used for cisterns. This homogeneity of proportions, which can be found from the beginning of the eighteenth century to the nineteenth, contrasts with that published in literature, where ratio was 1:1, based on archival materials preserved in the UST Archives [5].

From these dispersed historical data, it can be inferred that walls of stone and brick were common in Manila during the eighteenth century, although probably not prior or after that period. Chinese traditional bricks are described in the Yingzao Fashi (11th century) [14]. Although there are several types depending on their function, one of them is around 14.1 × 14.1 × 4.7 cm, considering 1 chi = 23.5 cm (0.6 × 0.6 × 0.2). Apart from this pattern, other bigger and flatter proportions are described in Chinese sources and can be found in earlier building constructions in the Philippines (i.e. Santa Ana de Sapa or Nagcarlan churches). Such variety is not so wide in Spanish tradition, being usually 29 × 14 × 4 cm in the eighteenth century [15], while nineteenth century engineers in Manila defined them as 24 × 12 × 5 cm. Despite this, in Europe it is traditional to cut bricks, which would give two halves of 14 × 14 × 4 cm. Regarding mortars, budgets clarify that 1:3 relation of lime and sand were common, while other organic ingredients could be included. Correspondence 1:3 seems to be not common in other territories under the Spanish administration, apart from nineteenth century Cadiz [16]. For example, in nineteenth century Havana, 2:3 was found, while in Puerto Rico was 2.5:3. These options were closer to that proposed from previous studies (2:3), and common in Europe [17]. On the other hand, the usual mortar in China during Ming and Qing dynasties was the sticky-rice variety [18]. It was manufactured from sticky rice soup and burnt lime creating a sturdy mortar material. Both in Macao and Manila in that time, lime production was under Chinese control and the possibility of traditional knowledge transfer is probable. On the contrary, oyster shell lime was produced in both Iberian settlements under the name chunam a similar term which can be found in Sanskrit as cuṇṇam [19]. Its original use in India included proportions from 1:1.5 to 1:3, but a substantial part of the mixture was jaggery water, a solution of molasses or coarse sugar, which was considered to facilitate the reaction of lime and sand due to the saccharine acid [20]. From all these options, Philippine artisans had the liberty of following a previous tradition, or create their own unique idea based from readily available materials. This is something difficult to confirm by relying only on historical texts.

The building of San Francisco (Manila) from historical sources and remains

Intramuros, the walled city of Manila, was built by the Spanish government in 1571. Despite the area being occupied previously by local chieftains, built tangible remains can only be traced from the sixteenth century onwards. The San Francisco convent occupied a big plot of land on the east section of
Intramuros since the beginning of the Franciscan’s mission in the Philippines. The mission’s first structure was built in 1577 [21]. In 1602 the friars were able to rebuild the entire complex in stone walls and wooden roof. This structure was generally preserved until the eighteenth century with few incorporations such as a low tower at the rear part of the building. From 1741 the Franciscans asked the sangley Juan Tiongco and Juan Carmelo to design a new building [22]. Managed by these architects, Asian construction techniques may have been preferred. Unfortunately, the breakdown of expenses for the building materials used were not preserved, but information about the structure’s foundations were recorded in detail. The new structure was supported by an underground perimeter of $2 \times 2.5$ fathoms (3.66 m x 4.6 m) [23]. East section of the church, where the presbytery was located, followed the same measurements but preserving the remains of the old tower and including two specific buttresses, resulting to a foundation of 1.5 feet x 8 fathoms and 1 foot (0.45 m x 14.9 m). Such platform contrasts with the lineal display of most of the foundations of the building. The structure was severely damaged during the Word War 2 bombardment of Manila in 1945. The surviving remains were eventually demolished when Mapúa University bought the site after the war. Despite the church is no longer preserved, some foundation remains have been identified recently, allowing their chemical analysis. Based on the location where the samples were retrieved, it seems probable that the bricks and lime mortars corresponds to the lateral foundations, and not to the presbytery ones.

### Methods

#### Sampling

The samples used for chemical analysis were acquired from the foundational ruins of the former San Francisco Church, Intramuros, Manila, Philippines in 2014 (Fig. 1). Proper permission was granted by the Mapúa University to obtain these samples. Four attached red-colored bricks with the corresponding lime mortar were taken from the collection site. Each of the bricks were clearly identified having very similar measurements of $[1^{st}]$ 15.6cm x 14.0cm x 3.2cm; $[2^{nd}]$ 15.0cm x 13.5cm x 3.5cm; $[3^{rd}]$ 15.0cm x 13.5cm x 3.2cm; and $[4^{th}]$ 14.0cm x 12.8cm x 3.5cm, respectively. These size patterns have not been found in European architecture of that period either on walls or in foundations. However, it was described in China for use on city walls, although it is more related to the flooring material. Similarities with Yingzao fashi pattern led to the assumption that the preferred brick model was Chinese. A white to grayish-white colored lime mortar material with an average height if 1.4cm to 1.6cm is found between the brick samples.

#### Brick and mortar material

A representative brick sample (BRK) with an attached mortar (MTR) material (Fig. 2a) was subjected to the different chemical analysis described in this study. Three brick and mortar subsamples were gently removed from the two opposite lateral corners labelled as BRK-1, MTR-1, BRK-2 and MTR-2 shown in Fig. 2b and 2c and one in the middle segment section labelled as BRK-3 and MTR-3 in Fig. 2d, respectively. This method of subsampling was chosen to account for the distribution of the chemical components.
within the sample and to have a better understanding of its original manufacturing process. To prevent any contamination from the surrounding materials, each subsample was scrapped-off at a depth of approximately 0.5 to 1.5 cm from the exposed surface. BRK-1 and BRK-2 both have a reddish brown color while BRK-3 is colored dark reddish brown. The mortar subsamples all have grayish-white colors.

**Analytical Methods**

**Energy Dispersive X-Ray Fluorescence (EDXRF)**

A portion of the brick and mortar subsamples, BRK-1, BRK-2, BRK-3, MTR-1, MTR-2 and MTR-3 were analyzed using a Shimadzu EDX-7000, Energy Dispersive X-Ray Fluorescence Spectrometer (EDXRF). The samples were mounted individually on a polypropylene cup. A detailed analysis mode was carried out in a vacuum atmosphere having a collimator setting of 3 mm. The background was adjusted relative to CO\(_2\) due to the presence of large amounts of carbonates in the samples with a wavelength of radiation from 0.10 to 10.0 nm. This was reported as the loss of ignition (LOI). Total analysis time per sample is almost 5 minutes.

**Fourier Transform Infrared Spectroscopy (FTIR)**

The subsamples taken from the brick and mortar sample was prepared for FTIR analysis using the KBr pellet method in approximately 1:3 ratio of sample with anhydrous KBr powder. The pressed pellets formed were analysed using a Thermo Scientific Nicolet 6700 FT-IR Spectrophotometer over the mid-infrared region (4000 cm\(^{-1}\) to 400 cm\(^{-1}\)) in transmission mode. The samples were repeatedly scanned for 16 times at a resolution of 4 cm\(^{-1}\).

**Scanning Electron Microscope (SEM)**

The changes in the microstructure of the brick and mortar samples were investigated using a JEOL 5300 Scanning Electron Microscope (SEM). Fragments from the subsamples measuring about 3.00 mm in length were placed on a sample holder using a carbon tape for a stable mount. To make the sample more conductive, it was coated with a thin layer of gold for about 30 minutes. The SEM image was obtained through a spot-profile and back scattered electrons mode with magnifications for analysis taken at 1,500x and 5,000x.

**Protein Analysis of Albumen in Lime Mortars**

**Extraction of Protein**

Possible proteinaceous compounds in albumen added to the lime mortar samples were extracted utilizing the protocols of a similar protein determination study on mortars [24]. The extraction solvent was prepared by mixing 1.30 mL of 0.50 M Tris-HCl buffer (pH 6.8) and 5.00 mL of 0.867 M SDS with 0.0150 g of dithiothreitol in a 50 mL volumetric flask, followed by dilution to the mark with distilled water. A 1.00 g of ground mortar samples, MTR-1, MTR-2 and MTR-3 were extracted individually with 5.00 mL of
extraction solvent. Each mixture was sonicated thrice (15 minutes each), incubated for an hour at 56°C, followed by another sonication step (15 minutes) and centrifuged (3 minutes). The extracted mortar samples were stored at 4°C prior to analysis.

### Qualitative Tests for Ovalbumin Protein

The extracted mortar samples, MTR-1, MTR-2 and MTR-3 were subjected to the following qualitative tests; Xanthoproteic, Ninhydrin and Biuret Tests [25]. Egg whites (albumen) were used as the positive control and was prepared by dilution to a 1:10 ratio of distilled water. Ovalbumin is the dominant protein found in egg whites or albumen and should indicate a positive color as in reacts with the different tests. Distilled water served as the negative control. The extracting solution was also tested to determine if contaminations were originally present in the sample mixture.

For the **Xanthoproteic Test**, 10 drops of the extracted mortar solution were mixed with 5 drops of concentrated HNO\(_3\) and placed in a boiling water bath for 5 minutes. After cooling the solution to room temperature, 20% NaOH was slowly added drop-by-drop until a persistent yellow color develops. In a second batch of extracted mortars, the **Ninhydrin Test** was performed by combining 20 drops of samples with 10 drops of 0.1% ninhydrin solution and immersed in a boiling water bath for 2 minutes. The mixtures were cooled to room temperature until a purple color appears. The **Biuret Test** was done by preparing a third batch of extracted mortar and mixed with 10 drops of 10% NaOH. After which, 1 drop of 0.1% CuSO\(_4\) were added. A dark purple color should develop upon cooling.

### Quantitative Tests for Ovalbumin Protein

The Biuret and Bradford Assays were employed to quantify the amount of ovalbumin in MTR-1, MTR-2 and MTR-3. Two different concentrations of ovalbumin stock solutions, 10.0 mg/mL for the Biuret Assay and 1.0 mg/mL for the Bradford Assay, were individually prepared by dissolving standard ovalbumin powder (Sigma Aldrich, analytical grade) with distilled water in two separate 100 mL volumetric flasks. Both solutions were stored in 4°C until ready to use. The Biuret and Bradford reagents were prepared based on establish protocols in literature for protein analysis [26, 27]. Standard calibration curves for the two assays were constructed with varying concentrations of the ovalbumin stock solutions. Specifically, the concentration ranges from 0.050 mg/mL to 0.500 mg/mL (i.e. 0.050, 0.100, 0.150, 0.250 and 0.500 mg/mL) in a 1.00 mL solution for the Biuret Assay, and for the Bradford Assay, the range is from 0.100 μg/μL to 1.000 μg/μL (i.e. 0.100, 0.200, 0.400, 0.600, 0.800, 1.000 μg/μL) diluted to a total volume of 100 μL each, respectively. The sample blank for both assays is distilled water.

The Biuret reagent (4.50 mL) was added individually to each diluted ovalbumin stock solutions and to the extracted mortar samples (1.00 mL). These were allowed to stand for 15 minutes at room temperature (25°C) before determining the concentration. Similarly, Bradford reagent (5.00 mL) was mixed gently with another batch of diluted ovalbumin stock solutions and 50.0 μL mortar samples diluted to 100 μL in water. After 5 minutes, the absorbance readings were done. Absorbance readings were set at 545 nm for the Biuret Assay and 595 nm for the Bradford Assay, respectively using a Hitachi U-2000 UV-Vis
Spectrophotometer. The concentrations of ovalbumin in MTR-1, MTR-2 and MTR-3 were computed from the equation of the line.

Results And Discussion

Clay Brick

Quantitative elemental composition

Clay and sand are the general raw materials utilized in brick making. The individual percentages of the brick subsamples shown on the EDXRF data in Table 1 has a consistent and regular distribution pattern of elements in the entire brick material. Hence, the mean composition was considered for the analysis. The most abundant mineral component is SiO$_2$ averaging to more than half of the total percentage of elements in the sample at 53.508%. This value accounts for the SiO$_2$ naturally found in the raw materials as phyllosilicates (clay), quartz and feldspars. The SiO$_2$/Al$_2$O$_3$ ratio of 3.095% suggests a relatively less clay mineral and feldspar content compared to quartz. Possible illite or muscovite and K-feldspars are attributed to K$_2$O (1.256%). The amount of MgO (1.402%) implies that dolomite and clay minerals such as smectite and chlorites may be present in the sample. The CaO (2.743%) content indicates that the sample is composed of non-calcareous clay type. A CaO concentration that is less than 6.0% is considered as non-calcareous, while higher than 6.0% is a calcareous clay [28]. These clay types influence the formation of certain type of firing minerals as the temperature increases [29].

The total quantity of the flux materials in the sample (i.e. K$_2$O, Fe$_2$O$_3$, CaO, MgO and TiO$_2$) equals to 14.721% and was classified as a low refractory clay due to the total percentage of greater than 9.0% [30]. This property enabled the brick to vitrify at a lower temperature during firing [31]. The existence of Fe$_2$O$_3$ reveals the presence of hematite and magnetite. Due to the brick sample’s red color, it is likely that hematite is more dominant compared to magnetite which produces a black colored ceramic. Hence, this is an indication of an oxidizing atmosphere during the firing process. The high content of Fe$_2$O$_3$ which averages at 8.468% makes the brick sample suitable for structural related purposes [32]. The high value for the loss on ignition (LOI) at 13.562% is probably due to the presence of carbonates and clays fired at low temperature [33].
Table 1
Chemical analysis of brick subsamples with EDXRF

| Elemental Components | Percentage Composition (%) | BRK-1 | BRK-2 | BRK-3 | Mean |
|----------------------|-----------------------------|-------|-------|-------|------|
| SiO₂                 |                             | 51.256| 48.515| 60.753| 53.508|
| Al₂O₃                |                             | 15.992| 15.949| 19.930| 17.290|
| Fe₂O₃                |                             | 7.765 | 6.969 | 10.671| 8.468 |
| CaO                  |                             | 3.040 | 2.123 | 3.065 | 2.743 |
| MgO                  |                             | -     | 2.033 | 2.174 | 1.402 |
| SO₃                  |                             | 1.169 | -     | -     | 0.390 |
| K₂O                  |                             | 0.163 | 1.083 | 1.523 | 1.256 |
| TiO₂                 |                             | 0.767 | 0.721 | 1.065 | 0.851 |
| MnO                  |                             | 0.162 | 0.135 | 0.385 | 0.227 |
| P₂O₅                 |                             | 0.115 | 0.109 | 0.257 | 0.160 |
| SrO                  |                             | 0.047 | 0.040 | 0.059 | 0.049 |
| V₂O₅                 |                             | 0.044 | 0.039 | 0.054 | 0.046 |
| ZnO                  |                             | 0.019 | 0.012 | 0.019 | 0.017 |
| Cr₂O₃                |                             | 0.150 | 0.010 | 0.014 | 0.058 |
| ZrO₂                 |                             | 0.110 | 0.012 | 0.016 | 0.046 |
| Ir₂O₃                |                             | 0.004 | 0.004 | 0.006 | 0.005 |
| LOI                  |                             | 18.43 | 22.245| 0.010 | 13.562|

*LOI – lost of ignition

Qualitative mineralogical characterization
The FTIR spectral features of BRK-1, BRK-2 and BRK-3 are almost identical. This implies that the raw materials used in manufacturing the brick are similar and it was mixed homogenously. Studies have shown that the common minerals present in historical bricks, which is generally derived from clay and sand materials, are quartz, feldspars and the phyllosilicate clay minerals such as kaolinite, illite and montmorillonite [34, 35, 36]. Quartz is naturally mixed with clay or added intentionally as a temper. It has
a characteristic infrared peak ranging from 900 to 1200 cm\(^{-1}\) [37]. As shown in Fig 3, the brick sample has an intense broad band centered at 1090 cm\(^{-1}\) and assigned to the Si-O asymmetric stretching vibration. Clay minerals are also composed of Si-O sheets and vibrate strongly at this wavenumber causing signals to overlap with quartz. Furthermore, the existence of quartz is supported by the Si-O symmetric stretching (\(\nu_1\)) at 789 cm\(^{-1}\), and Si-O symmetric (\(\nu_2\)) and asymmetric bending (\(\delta_4\)) at 694 cm\(^{-1}\) and 465 cm\(^{-1}\), respectively [38].

Besides having similar Si-O stretching vibrations with quartz, clay minerals are identified based on the characteristic OH stretching modes ranging from 3400 to 3750 cm\(^{-1}\) [39, 40], as shown from the broad peak centered at 3440 cm\(^{-1}\). Natural clays are usually composed of different clay minerals with minor structural differences hence, it absorbs together and appearing as a broad peak in the spectrum. The OH stretching bands due to the absorbed water also contribute to the peak intensities within this region. The presence of 2:1 layered type clay silicates such as illite and montmorillonite is attributed to the tetrahedral bending modes at Si-O-Si at 428 cm\(^{-1}\) and the OH bending frequency of Fe\(^{III}\)-Al\(^{III}\)-OH at 879 cm\(^{-1}\) [41]. Aluminum in the octahedral sheet of clay is supported by the Al-O coordinate vibration at 654 cm\(^{-1}\) [42]. Furthermore, the typical water absorption of montmorillonite in its crystal lattice is seen from the OH bending vibration at 1620 cm\(^{-1}\) [37].

The feldspar content in the brick sample is associated with the multiple broad and overlapping spectral features distributed within the range of 420 to 780 cm\(^{-1}\) and 1010 to 1170 cm\(^{-1}\) [43]. Carbonate minerals identified as calcite is also present based on the peak at 1450 cm\(^{-1}\) and assigned to the C-O asymmetric stretching (\(\nu_3\)) [12]. The other distinct carbonate ion vibrations are not readily distinguished from the spectra due in part to its low concentration compared to the other minerals in the sample. It may have been possible that the carbonate minerals were either added unintentionally during the manufacturing processes or are primary minerals in the clay. The formation of post firing minerals specifically hematite (Fe\(_2\)O\(_3\)) and magnetite (Fe\(_3\)O\(_4\)) were established based on the bands at 536 cm\(^{-1}\) and 579 cm\(^{-1}\), respectively. All the bands observed in the FTIR spectrum agrees well with the characteristic absorption patterns for old clay brick materials in the Philippines [40].

**Estimation of firing temperature**

FTIR technique was used to determine the lower limit of the brick’s firing temperature during manufacture and the condition of the kiln’s environment throughout this process. The thermal changes of the minerals in the raw material is a good indication of the possible firing temperature. The intense broad peak at 1090 cm\(^{-1}\) shown in Fig. 3 is the result of the dehydroxylation and eventual breaking of the aluminum octahedral sheet structure originating from the disappearance of well-defined peaks at 1100 cm\(^{-1}\) (Si-O stretching) and 915 cm\(^{-1}\) (inner hydroxyl bending) in pure clays. The formation of this intense peak will occur as the temperature reaches 650°C [44]. The weak band at 879 cm\(^{-1}\) is also an indicator of the maximum extent of collapsing exhibited by the octahedral sheet in clay minerals. Its presence signifies incomplete dehydroxylation of the clay in the sample which is attributed to a firing temperature below
800°C [45]. This possible higher temperature limit of 800°C is further supported by the existence of undecomposed calcite (1450 cm⁻¹) which will begin to turn into carbon dioxide gas and disappear at temperatures starting 800°C [46].

The presence of post firing minerals specifically when aluminum is replaced by iron in the clay sheet structure to form hematite and magnetite, will begin to develop at a temperature above 600°C. This shows that the brick sample may have a lower temperature limit of 600°C which is supported by the disappearance of the octahedral sheet layer as discussed above. As the temperature continue to rise, the intensities of the bands for hematite (536 cm⁻¹) and magnetite (579 cm⁻¹) also increases and usually form stable mineral structures at a temperature higher than 700°C [45] as shown in Fig. 3. The band for hematite (536 cm⁻¹) is a good indicator that the brick sample may have been fired at an oxidizing atmosphere. This is further supported by the dark reddish color of the sample. This implies that the brick kiln is saturated with available oxygen during the firing process or may have been fired in an open-air environment [30]. Based on these FTIR results, it can be inferred that the brick sample may have been fired at a temperature between 600°C to 800°C in an oxidizing atmosphere.

Information on the brick’s microstructure utilizing SEM further confirmed the possible firing temperature. Classifications made from previous studies on clay potteries were applied on the sample to assess the microstructural changes inside the brick. Both clay bricks and potteries will have the same mineralogical changes as the temperature increases. As shown in Fig. 4a and b, the process of sintering is gradually occurring and there are interconnections already forming between the phyllosilicates and the non-plastic components such as quartz. The existence of isolated pores measuring from 2.5 to 3.5 μm are consistent for a clay material that is fired at a low temperature and in an oxidizing atmosphere (Fig. 4a). Thus, agreeing well with the results of the FTIR and EDXRF. An earlier stage of vitrification classified in the literature as NV+, which is a type of vitrification stage in-between the no vitrification (NV) to the succeeding stage of initial vitrification (IV), is assigned to the sample [47, 48]. These observations are based on the slight deformation of the clay plates into round edges and the absence of well-defined smooth glassy filaments on the microstructure seen in the SEM image (Fig. 4a and b). Results of the SEM together with the EDXRF (i.e. non-calcareous and low refractory) implies a firing temperature of ≤ 800°C [30].

**Lime Mortar**

**Quantitative elemental composition**

Historical accounts in the Philippines reveals that lime used for binders in mortar preparations can either be sourced from limestone or seashells [5]. This will eventually be burned and combined with aggregates such as sand to form the lime mortar. Results from the EDXRF data in Table 2, shows that the lime raw material used in the sample is mainly calcitic (29.427 %) due to the absence of magnesium. This points to the possibility that the lime may have originated from crushed seashells. The amount of SiO₂, Al₂O₃ and Fe₂O₃ represent the aggregates mixed with the lime and as pozzolans burned together with the lime
material during calcination. These minerals are derived from sand containing mostly quartz, feldspars and phyllosilicates (clay) or probably crushed clay materials as observe from the Fe$_2$O$_3$ content (1.925 %) of the sample [12]. The SiO$_2$/Al$_2$O$_3$ ratio of 4.768 % also shows that quartz is relatively more dominant than clay particles implying that clays are minor additives in the mortar mixture. An approximate binder to aggregate ratio employed in the manufacturing process is obtained by generally comparing the amount of CaO (lime binder) with SiO$_2$ (sand aggregates). The CaO/SiO$_2$ ratio of 2.870 (approximately 3) implies that for every 1-part lime there is approximately 3-parts sand. Variations in the EDXRF data across the samples are attributed to the inhomogeneity in applying the lime mortar on the brick material.

The hydraulic behavior was measured by computing the cementation index (CI) using equation 1. In general, the more hydraulic the binder, the higher the value for CI. Based on the average EDXRF values of the different variables in the equation, the sample has a CI value of 1.104 and classified as a hydraulic lime mortar [49]. Hence, the mortar sample will set by reacting with water and pozzolans (i.e. clay or sand) are added together with the lime during the calcination process besides the aggregates. Hydraulic mortars are effective for external or structural purposes due to its binding strength.

$$[1] \text{CI} = (2.8) (\% \text{SiO}_2) + (1.1) (\% \text{Al}_2\text{O}_3) + (0.7) (\% \text{Fe}_2\text{O}_3)$$

$$\% \text{CaO} + (1.4) (\% \text{MgO})$$
Table 2
EDXRF results of the mortar samples

| Elemental Components | Percentage Composition (%) | MTR-1 | MTR-2 | MTR-3 | Mean |
|----------------------|---------------------------|-------|-------|-------|------|
| CaO                  |                           | 27.588| 18.681| 42.011| 29.427|
| SiO$_2$              |                           | 9.721 | 7.595 | 13.496| 10.271|
| Al$_2$O$_3$          |                           | 2.013 | 1.402 | 3.046 | 2.154|
| Fe$_2$O$_3$          |                           | 1.733 | 1.824 | 2.218 | 1.925|
| K$_2$O               |                           | 0.297 | 0.209 | 0.410 | 0.305|
| TiO$_2$              |                           | 0.118 | 0.080 | 0.188 | 0.129|
| SrO                  |                           | 0.080 | 0.038 | 0.122 | 0.080|
| SO$_3$               |                           | 0.190 | 0.065 | 0.070 | 0.108|
| V$_2$O$_5$           |                           | 0.022 | 0.010 | 0.025 | 0.019|
| ZrO$_2$              |                           | 0.006 | 0.003 | 0.008 | 0.006|
| CuO                  |                           | -     | -     | 0.008 | 0.003|
| ZnO                  |                           | 0.039 | 0.006 | 0.005 | 0.017|
| LOI                  |                           | 58.154| 70.050| 38.332| 55.512|

* LOI – lost on ignition

Qualitative mineralogical characterization

Identical FTIR absorption features were observed for the lime mortar samples, MTR-1, MTR-2 and MTR-3 and a representative spectrum is shown in Fig. 5. This indicates that the mortar preparation and the raw materials are similar across the samples. In the Philippines, lime used for binders are sourced from either limestone or seashells (i.e. oysters) which are mainly composed of calcium carbonate (CaCO$_3$). Consequently, prominent characteristic peaks of CaCO$_3$ in the form of calcite are seen from the spectrum by the intense C-O bending vibrations at 714 cm$^{-1}$ (in-plane, 4) and 876 cm$^{-1}$ (out-of-plane, 2), respectively, and the broad C-O asymmetric stretching vibration at 1430 cm$^{-1}$ (3). These are further supported by the combination modes at 1800 cm$^{-1}$ (1 + 4) and 2510 cm$^{-1}$ (2 + 2 + 4), and also by the peaks at 2870 cm$^{-1}$ and 2980 cm$^{-1}$ which are attributed to the overtones and 3 combination bands, respectively [50, 51].
Another component of mortars are the aggregates which in the case of the sample is comprised mainly of sand particles. The broad peak at 1030 cm$^{-1}$ shown in Fig. 5 is an indication of the Si-O asymmetric stretching vibration attributed to quartz. Other peaks to support the presence of quartz includes the Si-O symmetric stretching (1) at 779 cm$^{-1}$ and the Si-O bending vibrations at 646 cm$^{-1}$ (symmetric, 2) and 466 cm$^{-1}$ (asymmetric, 4), respectively [12, 52]. Clay minerals are also evident in the mortar sample as part of the natural impurities in limestone or included in the sand aggregates. Possible examples of which are the clay minerals hematite and montmorillonite, assigned to the weak peaks at 523 cm$^{-1}$ and the OH bending vibration at 1620 cm$^{-1}$, respectively. Absorbed water in the interlayer of the clays’ silicate and aluminate hydrates are represented by the broad OH stretching band centered at 3420 cm$^{-1}$ [12].

Microstructural evaluation

The lime mortar’s SEM image (Fig. 6a and b) shows that the binder is composed of fine crystalized calcite and are well carbonated [53, 54]. This implies a high conversion rate of slaked lime or Ca(OH)$_2$ to calcium carbonate by reaction with atmospheric CO$_2$ through time. The presence of aggregates embedded on the binder matrix is observed from the SEM image of MTR-1 (Fig. 6a). Furthermore, MTR-3 shows the typical fiber patterns of precipitated calcium silicate hydrates which facilitated the hardening process of the mortar [55]. The microstructure is also considered as well packed and have less pores (Fig. 6b). These characteristics contributed to the sturdiness of the physical structure of the lime mortar.

Qualitative and quantitative tests for proteins

Accounts of egg whites or albumen and other organic compounds such as plant extracts and molasses have been used as additives in lime mortars to improve the binding abilities and material strength [5]. About 60% of the total weight of the egg is made up of albumen. From this percentage, proteins and water are the major components. Since ovalbumin (54%) mainly comprise the protein part, it has the highest possibility of being extracted in the mortar samples and detected through the chemical tests [56]. The qualitative tests performed on the extracted mortars, MTR-1, MTR-2 and MTR-3 are intended to assess the different amino acids in the ovalbumin protein structure. Xanthoproteic Test detects the presence of aromatic groups in amino acids, the Ninhydrin Test for the presence of 1°,2° and free amines, and the Biuret Test for the determination of two or more peptide bonds in the amino acid sequence of ovalbumin, respectively.

Fig. 7 a, b and c shows the distinct color produced by the reaction of the different qualitative tests with a positive control made from diluted egg white in water. The Xanthoproteic Test yields a distinct yellow colored solution, a purple colored solution was observed for the Ninhydrin Test, and the Biuret test produced a deep blue-violet colored solution. Similarly, the negative control consisting of distilled water was also tested as well as the solution used for extracting the lime mortar samples. The absence of the characteristic positive colors in these solutions indicates that there are no contaminations that may lead to a false positive result.
It can be seen from Fig. 7 that the mortar samples, MTR-1, MTR-2 and MTR-3 remained colorless upon the addition of the Xanthoproteic Test reagents instead of the yellow colored solution expected for a positive result. This indicates that there are no amino acids with aromatic groups in the samples. Furthermore, none of the mortar samples exhibited the distinct positive purple color that would have been produced by the reaction of 1°, 2° and free amines with Ninhydrin compound. Instead, a light sky-blue colored solution was produced which implies that these amines are not present in the extracted mortar samples. A more general test for proteins is the Biuret test and the mortar samples produced a cyan colored solution as it reacts with the Biuret reagents. This demonstrates the absence of compounds that have peptide bonds in samples.

The negative results produced in all the qualitative tests made on MTR-1, MTR-2 and MTR-3, may suggests the possibility that no albumen was originally added to the lime mortar sample during its manufacture or the concentration of the ovalbumin peptide fragments may not be enough for the reaction to be detected by the color tests. Moreover, the albumen proteins may have also degraded through time due to its exposure to the environment and microbial growth [10].

Further confirmation of the qualitative results was done by identifying the amount of protein fragments quantitatively using the Biuret and Bradford Assays in UV-vis spectrophotometer. Both assays offer the advantage of being rapid, simple and with fine sensitivity. For the quantitative tests, a standard calibration curve using an ovalbumin standard solution was initially constructed for comparison to the possible ovalbumin fragments in MTR-1, MTR-2 and MTR-3. The individual absorbance readings for both assays relative to the series of standard concentrations prepared was plotted with regression lines of $R = 0.9953$ (Biuret assay) and $R = 0.9964$ (Bradford assay). The equation of the line was determined from the graph to be equal to: $y = 0.0261x + 0.0231$ for the Biuret Assay and $y = 0.1834x + 0.0364$ for the Bradford Assay, respectively. These equations were used to compute for the concentration of the possible protein fragments in the mortar samples.

Table 3, summarizes the results of the quantitative tests for MTR-01, MTR-02 and MTR-03. Negative valued concentrations were computed from the two assays indicating that no ovalbumin fragments were detected by the assays. Hence, egg whites are possibly absent in the lime mortar samples.

| Lime Mortar Samples | Biuret Assay (mg/mL) | Bradford Assay (mg/mL) |
|---------------------|----------------------|------------------------|
| MTR-1               | -0.234               | -0.156                 |
| MTR-2               | -0.195               | -0.150                 |
| MTR-3               | -0.157               | -0.161                 |

Conclusions
The use of chemical analysis has broadened the understanding of the provenance and manufacturing process employed in the Spanish Period in the Philippines. Bricks were manufactured from the combination of sand with non-calcareous and low refractory clays. It was fired at a temperature between 600 °C to 800 °C in an oxidizing atmosphere. Regarding the measurements of the brick, there are Chinese models close to the Philippine sample, although they are also used in Spanish or American works as half bricks.

The attached lime mortar is calcitic, well carbonated and the lime may have originated from crushed seashells. Clay tempers or sand may have been added to strengthen the workability of the material due to its hydraulic lime nature. The lack of organic additives specifically egg albumen may indicate a different form of mixture compared to sticky-rice mortar (chunam) or other European solutions. Proportions were also unlike foreign traditions but coinciding with those described in the Philippines. It can be considered that local architects chose a model which was similar to their traditions.

The Philippine builders were already familiar with traditions from India, China, America and Europe, but opted to prioritize methods based on available local materials and skills. Both historical and chemical results do not support the adoption of any of the previous construction techniques, either Western or Eastern, apart from the measurements of bricks, which was reinterpreted from their own perspective. Further analyses will allow to confirm if eggs, rice straws or honey were added as foreign improvements as some historic sources indicate.

**Abbreviations**

UST: University of Santo Tomas (in Manila, Philippines); EDXRF: Energy dispersive x-ray fluorescence; LOI: loss of ignition; FTIR: Fourier transform infrared spectroscopy; SEM: Scanning electron microscope; NV: no vitrification; IV: initial vitrification; CI: cementation index; UV-Vis: Ultraviolet-visible spectrophotometer.

**Declarations**

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**Competing interests**

The authors declare that they have no competing interests.

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**Figures**

![Figure 1](image_url)

**Figure 1**

Foundation ruins of the former San Francisco Church. Sampling site where the brick and mortar samples for chemical analysis were collected.
Figure 2

(a) Sample material used for chemical analysis, (b) and (c) are the portions of the lateral corners where BRK-2, MTR-2, BRK-3, and MTR-3 were taken, and (d) BRK-3 and MTR-3 are the inner middle section of the sample material.
Figure 3

FTIR spectrum of a representative brick subsample in the mid-infrared region

Figure 4

SEM microstructure image of (a) BRK-1 at 1,500x magnification (b) BRK-3 at 1,500x magnification

Figure 5
FTIR spectrum of a representative mortar subsample in the mid-infrared region

**Figure 6**

SEM microstructure image of (a) MTR-1 at 5,000x magnification (b) MTR-3 at 1,500x magnification

**Figure 7**

Comparison of the positive control with the negative control, extracting solution and the lime mortar samples. (a) Xanthoproteic Test (b) Ninhydrin Test and (c) Biuret Test.