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Analytical Chemistry Methods of Estimating the Hydraulic Lime Characteristics of Mortars from a Spanish Colonial Period Fortification in the Philippines: Perspective of a Southeast Asian Country

Mga Pamamaraan ng Suriing Kapnayan sa Pagtantya ng Katangiang Haydroliko ng Apog sa Argamasa na Mula sa Isang Panahon ng Kastilang Kuta sa Pilipinas: Pananaw ng Isang Bansa sa Timog-Silangang Asya

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Abstract

This study provides an analytical chemistry method to reveal the production technologies employed in lime mortar making from a Spanish Colonial Period (16th to 19th century) fortification in Bacolod, Lanao del Norte, Philippines. The scarcity of baseline chemical data on Spanish Colonial Period lime mortars in the Philippines is addressed by utilizing analytical techniques such as Energy Dispersive X-ray Fluorescence (EDXRF) and Thermogravimetric analysis (TGA). The EDXRF and TGA effectively provided information on the chemical composition of the lime mortars and the hydraulic nature of the binder used. The two mortar samples (FA-1 and FA-2) from two different areas of the fort, are made of minerals containing calcium oxide (CaO, $< 31\%$), silicon dioxide (SiO_2, $< 12\%$), aluminum oxide (Al_2O_3, $< 4\%$) and iron (III) oxide (Fe_2O_3, $< 5\%$). Due to the lack of magnesium, both samples are classified as originating from calcitic lime of possibly marine shell origin. The hydraulic characteristic (CO_2/H_2O ratio) of FA-1 (1.06 % loss) and FA-2 (5.15 % loss) is due to clay additives suggesting that hydraulic mortar preparation already existed during that period. These analyses show the importance of systematic and detailed chemical data on Spanish Colonial Period lime mortars which can contribute to cultural heritage discourses in the Philippines.

Ang pag-aaral na ito ay nagbigay ng isang pamamaraan ng suriing kapnayan upang maipakita ang mga teknolohiya ng paggawa sa apog na argamasa mula sa isang kuta na itinayo noong panahon ng mga Kastila (ika-16 hanggang ika-19 na siglo) sa Bacolod, Lanao del Norte, Pilipinas. Ang kakulangan ng bantayang linya ng datos kemikal ng mga apog na argamasa nuong panahon ng mga Kastila sa Pilipinas ay tinalakay sa pamamagitan ng pagamit ng mga suriing pamamaraan tulad ng

Energy Dispersive X-ray Fluorescence (EDXRF) at *Thermogravimetric Analysis* (TGA). Ang EDXRF at TGA ay mabisang nagbigay ng impormasyon sa kapnayaning kasangkapan ng apog sa argamasa at ang haydrolikong katangian ng apog na ginamit. Ang dalawang uri ng argamasa (FA-1 at FA-2) na nagmula sa dalawang magkaibang lokasyon sa kuta, ay gawa sa lupangkap na naglalaman ng kalsyum oksad (CaO, < 31%), silikon daluksad (SiO_2, < 12%), aluminum oksad (Al_2O_3, < 4%), bakal (III) oksad (Fe_2O_3, < 5%). Sa kadahilangang walang magnisyum sa parehas na argamasa, maituturing ito na nagmula sa *calcitic* na apog na maaaring nanggaling sa mga kabibe sa karagatan. Ang haydrolikong katangian (CO_2/H_2O tagway) ng FA-1 (1.06 % ang nawala) at FA-2 (5.15 % ang nawala) ay dahil sa mga ihinalong luad na nagmumungkahi na meron nang kaalaman sa prosesong ito nuong panahon na iyon. Ang mga pagsusuring ito ay nagpapakita sa kahalagahan ng sistematiko at detalyadong datos kemikal sa mga apog na argamasa nung panahon ng mga Kastila na makakapag-ambag sa mga mahahalagang usapin patungkol sa kalinangan at pamanang yaman sa Pilipinas.

Keywords: lime mortar, EDXRF, TGA, hydraulic type, fortification, Spanish Colonial Period | apog na argamasa, EDXRF, TGA, haydroliko, kuta, Panahon ng Kastila

Introduction

The masonry bonded by lime-based mortar in the Southeast Asian region has a long history of usage, evident in the 9th century Chaiya monuments in Thailand (Dumarçay 2005) and the 13th century Me-taw-ya temple in Pagán Valley, Myanmar (Amadori et al. 2019). Besides mortars made of lime, other construction methods that predominate in the region include the adoption of a mortarless or dry-joint masonry method, as observed from Khmer temples in Cambodia (Apsara-UNESCO 2012), and the use of plant-based resin mortars such as in the Mỹ Són temples in Vietnam derived from the local dàu rài tree (Binda et al. 2006). In the context of the Philippines, widespread utilization of lime-based mortars occurred during the Spanish Colonial Period, as seen from the different ecclesiastical, secular, and colonial government structures that survived until this day.

Lime mortars have dominated construction work worldwide until replaced largely by concrete prepared from Portland cement in the late 19th to early 20th century. Even though lime-based mortar and Portland cement were both manufactured from calcium carbonate ($CaCO_3$), the difference mainly comes from Portland cement's added pozzolans, such as specific quantities of clay, volcanic ash, or sand, and fired consistently at a high temperature of almost 1500°C. These parameters produced different post-firing minerals with distinct chemical properties upon reaction with water that is not present in low temperature (i.e., less than 1000°C) fired lime in old mortars (Hall 1976). Hence, from the standpoint of good conservation practice, Portland cement is chemically incompatible with lime mortars found in historical, turn of the 20th century, structures.

Due to the lack of standardized manufacturing processes during the Spanish Colonial Period, preparing lime to make mortars varies depending on the builder's skills, the provenance of raw materials, manufacturing location, and the kiln or firing technology. Despite these variations, the main mortar components include the binder (i.e., lime, mainly $CaCO_3$), aggregates (i.e., crushed stones, broken seashells, or pottery), and water. Since the Philippines is archipelagic, it is believed that the lime source used for binder in those days were obtained from crushed corals and marine shells like oysters. It can also come from quarried limestones (Jose 2003). In the Lime Cycle (Elert et al. 2002; Hansen et al. 2008) process shown in Figure 1, the lime raw material is crushed and fired at a temperature greater than 600°C to remove carbon dioxide, CO_2, producing quick lime or calcium oxide, CaO. The firing was done using an intermittent kiln or open-air methods as reported in scientific literature, but no mention of the firing temperature range achieved (Reyes 1928). Water is added to CaO to produce calcium hydroxide, $Ca(OH)_2$, or slaked lime. Depending on the purpose of the lime, it can be prepared in either dry slaking or wet slaking techniques, where the former uses just enough water to slake it, while the latter uses more water for slaking (Balksten 2007). The mixtures produced are continuously soaked in water for at least three months. Once ready, the aggregates, usually river stones, are combined with the lime binder in specific proportions and applied between the masonry material. In time, the mortar will eventually dry out and react with atmospheric CO_2, forming back the original $CaCO_3$ composition. Interestingly, organic additives such as plant parts, molasses, and egg albumin are supposedly added to the lime-aggregate mixture to facilitate better cohesion and hardening, but no systematic scientific data has been reported yet (Jose 2003). Combinations of all these factors contribute to the quality and the physical and chemical properties of the mortars produced.

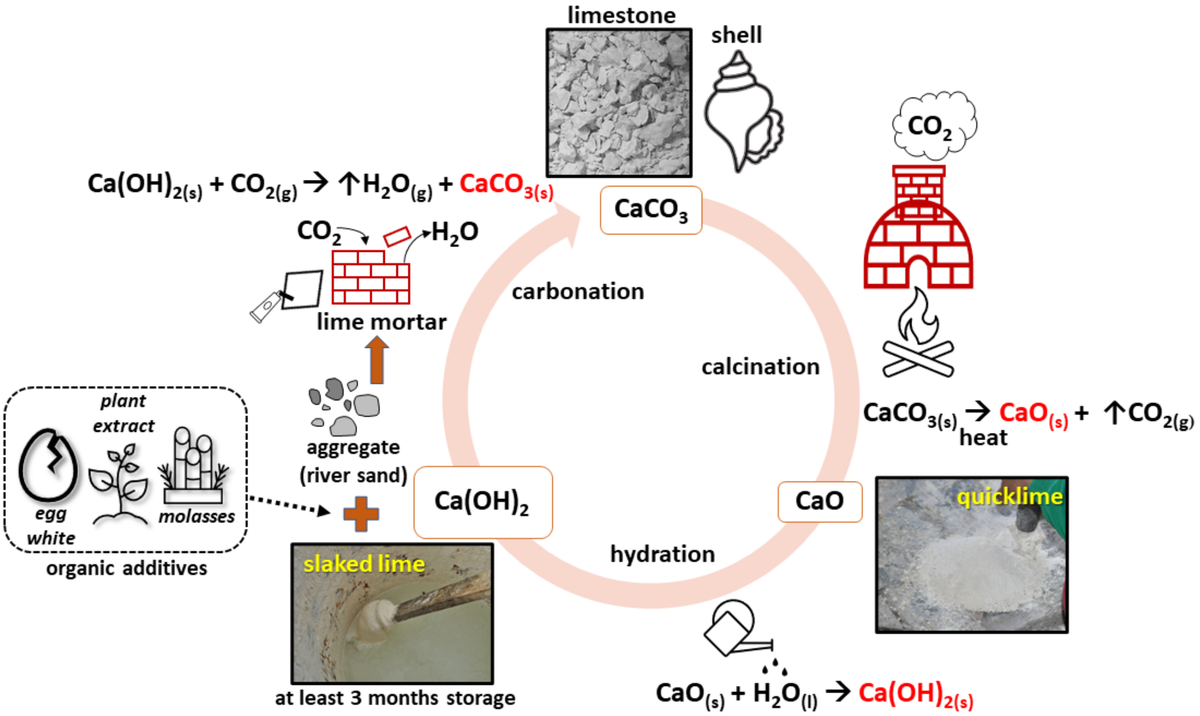

Fig. 1 General Lime Cycle process including the relevant chemical reactions and the possible association to the lime mortar production in the Philippines, based on Jose 2003. Source: Graphics and photos by JM Cayme.

The complexity of the lime mortar's chemical composition and the lack of substantial historical records on the technology employed during its production have made chemical analysis necessary to gain more information on its manufacturing method. Baseline chemical data on old lime mortars in Southeast Asian countries was reported from the Philippines, particularly from Christian church ruins in Manila (Cayme and Asor Jr 2016), Misamis Oriental (Cayme and Asor Jr 2017), Albay (i.e., Budiao and Cagsawa) (Laplana et al. 2018; Mangay et al. 2018), and a missionary chapel in Marikina (Cayme et al. 2018). Furthermore, chemical investigations were also applied on lime mortars for future conservation works of different ancient Buddhist temples (wats) and a palace in Bangkok and Ayutthaya in Thailand (Mahasuwanchai et al. 2020; Wonganan et al. 2021), and the Fort Cornwallis in Penang, Malaysia (Harun et al. 2002; Ismail et al. 2003). Proper restoration of structures heavily damaged by earthquakes from the Dauis Church in Bohol, Philippines (Kalaw and Naguit Jr 2019), and Bagan temples in Myanmar (Thet Mon San et al. 2018; Amadori et al. 2019) have benefitted from the elemental data of lime mortars originally used in these structures. These studies show that analytical chemistry techniques have tremendous potential for mainstream applications on heritage structures in the Southeast Asian regions, where scientific research remains very limited until today.

To fill the gap on historic lime mortar research in the Southeast Asian context, the hydraulic characteristics of lime mortars from a Spanish Colonial Period fortification located at Bacolod, Lanao Del Norte, Philippines is reported in this study. The binder's hydraulic behavior has something to do with its hardening action in the presence of water (i.e., hydration) besides the general lime cycle reactions in Figure 1. The more a binder sets through hydration, the more hydraulic it is. Consequently, the less it sets through water, it becomes non-hydraulic or a binder that would eventually harden more through carbonation or exposure to atmospheric CO_2 (Sabbioni et al. 2002). Hence, hydraulic lime is preferred for constantly exposed structures underwater or thick walls such as fortifications. The key to influencing the hydraulic properties in binders are minerals from burned clay or volcanic materials present naturally in the raw material or added intentionally during the manufacturing process (Moropoulou, et al. 1995b; Balksten 2007). Chemically, the formation of calcium silicate minerals from calcium hydrates in lime with clay minerals is responsible for hydraulicity (Ingo et al. 2004). About 10% to 15% clay fired with lime can provide a hydraulic mortar mixture (Torraca 2009).

The approach of this study is to combine two complementary analytical methods to investigate the type of lime binder in the mortar samples using the Energy Dispersive X-Ray Fluorescence (EDXRF) and the Thermogravimetric Analyzer (TGA). EDXRF provides a method for quantifying and identifying the elemental composition in the mortar and possible inorganic additives in the lime binder (Madariaga 2015). X-ray fluorescence (XRF) techniques, in general, have been shown in a study from Malaysia to be effective in assessing the binder and sand aggregate ratio for duplicating the old mortar mixture in a conservation project (Ling and Ahmad 2018). Restoration of damaged heritage structures in the Philippines (Kalaw and Naguit Jr 2019) and Myanmar (Thet Mon San et al. 2018) have also benefitted from the XRF technique by providing chemical data on the original mortar components before attempting any repairs. On the other hand, the TGA identifies the thermal transformation products and reactions during controlled heating of the mortar while monitoring the weight changes (Moropoulou et al. 1995b). Researchers have utilized this technique to classify the air-lime characteristics of a mortar sample from the Philippines (Cayme and Asor Jr 2016) and determine the $CaCO_3$ content of lime from a study in Myanmar (Amadori et al. 2019). Through the TGA, the difference between the original and restoration mortars in a temple in Thailand was uncovered and found to be of different types (Siedel et al. 2019). Thus, identifying the hydraulic nature of the binder with the aid of EDXRF and TGA will contribute to a more scientific understanding of mortar materials.

Fort Almonte and the Lime Mortar Sample

Records on the construction history of Fort Almonte in Bacolod, Lanao del Norte (Figure 2), presumed to be built in the late 1800s, are minimal. The fort was named in honor of Spanish Admiral Pedro Almonte, who in the early 1600s led a successful campaign against the Moros in the Philippines' southern island, Mindanao. It is located strategically at the estuary of the Iligan Bay and the Liangan river, which is today within the Liangan East Public Elementary School compound. The Liangan river is a crucial access point for Moro pirates in the Mindanao region. It necessitates control by the Spanish Colonial government to prevent the rampant piracy plaguing the other islands in the country during those days. It is a quadrilateral bastioned fort with palisades in some sections and moated (Figure 3). Like any fortifications in the Philippines, Spanish officers and an army composed of a few Spanish infantry and a large contingent of Filipino natives would typically guard the fort (Javellana 1997; Muog 2008).

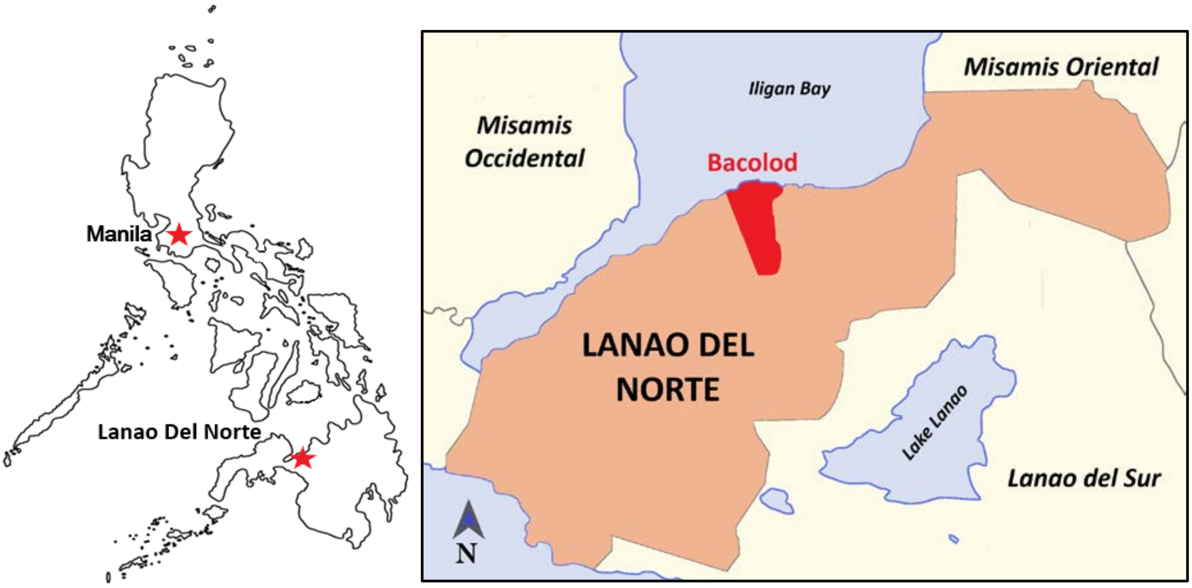

Fig. 2 Map of the Philippines showing the proximity of the Province of Lanao del Norte relative to the country's capital, Manila (left). Map of the Province of Lanao del Norte where the Municipality of Bacolod is approximately located (right). Source: JM Cayme.

Fig. 3 Fort Almonte within the Liangan East Elementary School, Bacolod, Lanao del Norte. The outer front wall (left) and the inside wall portion (right) view. Source: Photo by JM Cayme, April 2015.

Table 1 shows the lime mortar samples obtained in 2015 from selected portions of Fort Almonte and labelled as FA-1 and FA-2. The pieces were carefully removed between the joints of the coral stone walls using a chisel to obtain a total mass of approximately 2.0 grams each. These amounts were sufficient to perform the EDXRF and TGA analysis needed for this study and minimal enough to preserve the historical fabric of the structure. Upon collection, the mortar sample portion facing the exterior part, which is contaminated by the surroundings, was discarded to prevent conflicting information from the analyses. A closer inspection of the sample's physical properties confirms that it is made of old lime mortars and not modern-day cement.

Mortar Code	Mortar Type	Sampling Area	Approximate Sampling Location
FA-1	Joint mortar	Western side of the fort. Inner wall column.	
FA-2	Joint mortar	Southern side of the fort. Back portion of the stairway.	

Table 1 Sample mortar descriptions. Source: Photo by JM Cayme, April 2015.

Experimental Analytical Methods

An analytical instrument, Shimadzu EDX-7000, Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer, was utilized to determine the elemental oxide composition (in percentage) of the lime mortar samples. A small representative piece of the sample, enough to be accommodated in a standard polypropylene cup holder, was loaded into the EDXRF. Each analysis was done in a vacuum atmosphere and was programmed to perform a thorough “detailed-mode” scanning with a run time of about 5 minutes. The collimator size for the X-ray beams was set to 3 mm. Since lime mortars have calcium carbonate ($CaCO_3$) as the primary component, undetected elements like carbon dioxide and absorbed water are reported by the instrument as the loss on ignition (LOI).

Characterizing the lime mortar utilizing thermal analysis was performed on a Thermogravimetric Analyzer (TA Instruments Discovery TGA55). The samples were heated in the instrument at a controlled rate of 10°C per minute from 22°C to 1000°C in a nitrogen gas atmosphere. The instrument detected the weight losses of each sample having initial masses of 8.281 mg (FA-1) and 6.199 mg (FA-2), as the heating temperature increases. Due to the high-temperature upper limit (i.e., 1000°C), a platinum pan (Platinum HT) was used to hold the samples.

Results and Discussion

Quantitative elemental composition

Mortars are manufactured from a binder made of lime and aggregates, usually sand. This historical information is reflected from the results of the EDXRF data in Table 2, showing that FA-1 and FA-2 are abundant in calcium ranging from 30.3 to 30.5% CaO and silicates from 10.1 to 11.8% SiO_2, respectively. Lime is chemically made of calcium, while sand, in general, is composed of silicates due to the mineral quartz (SiO_2). The binder in both mortar samples is considered calcitic or mainly $CaCO_3$ instead of having a dolomitic, $CaMg(CO_3)_2$, character due to the absence of significant peaks for magnesium in the EDXRF (Cayme and Asor Jr 2016). These results imply that the lime raw material may have been sourced from coralline or marine shells rather than quarried limestones because dolomite is more common in rock minerals (Theodossopoulos 2012). Fort Almonte's very close proximity to bodies of water and located in an estuary makes this chemical assumption plausible. The quality of the $CaCO_3$ binder can also be assessed from the computed weight ratios of CO_2 compared to the LOI (loss on ignition) values. Since the molar masses of CaO and CO_2 are 56 g/mol and 44 g/mol, respectively, the percentage of CO_2 in FA-1 is 23.95%, and for FA-2, it is 23.81%. These values account for 44.14% (FA-1) and 49.76% (FA-2) of the LOI reported in the EDXRF for the individual mortar samples. Around 50 to 56% of the unaccounted LOI values may be attributed to organic matter and hydrated compounds, demonstrating that the carbonated binder was not entirely pure (Kang et al. 2019).

Two other major elemental oxides (> 1.0%), which are iron (Fe_2O_3) at 1.1 to 4.2% and aluminum (Al_2O_3) at 2.7 to 4.0%, respectively, were also detected by the EDXRF in both mortar samples (Table 2). These amounts provide valuable hints that clay minerals are likely involved as aggregates or additives in the original lime mixture. Combinations of silicon and aluminum are present in clay phyllosilicate minerals which are responsible for its plastic behavior and are either stacked in a 1:1 or 1:2 clay mineral type ratio. Feldspars, which also have silicon-aluminum bonds, are usually part of natural sand and clays. Furthermore, the percentage of Fe_2O_3 that are elements attributed to the minerals hematite or magnetite are known products of the firing process in clays (Cayme 2021). Hence, implying that clay was fired together with the lime during the production process.

Sample	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**SrO**	**SO_3**	**K_2O**	**TiO_2**	**MnO**	**LOI***
FA-1	30.484	10.169	2.796	1.176	0.402	0.291	0.273	0.120	0.015	54.264
FA-2	30.300	11.719	3.970	4.126	0.208	0.898	0.308	0.480	0.077	47.848

Table 2 Chemical composition of the lime mortar samples using EDXRF. The name of the chemical element bonded to oxygen to form the oxides are the following: Calcium (Ca), Silicon (Si), Aluminum (Al), Iron (Fe), Strontium (Sr), Sulfur (S), Potassium (K), Titanium (Ti), Manganese (Mn). LOI is the Loss On Ignition, which describes the volatile compounds.

The hydraulic characteristics of FA-1 and FA-2 were estimated by computing the cementation index (CI) in Equation 1 using the EDXRF data. It is inferred from the equation that the more clay minerals present, as represented by the element oxides, SiO_2, Al_2O_3 and Fe_2O_3, the higher the CI value, thus the more hydraulic the sample. With regards to this trend, the binder is classified according to the following CI values: aerial (< 0.3), low hydraulicity (0.3 to 0.5), moderate hydraulicity (0.5 to 0.7), and hydraulic (> 0.7). Based on the computed CI values of the mortar samples, FA-1 is 1.06 and FA-2 is 1.32, suggesting that both mortars are hydraulic, and the amount of clay is enough to cause this behavior (Gleize et al. 2009). It is also possible that the binders were both produced in the same batch and with the same techniques.

$$[1] \quad \text{Cementation index (CI)} = \frac{(2.8)(\%\ SiO_2) + (1.1)(\%\ Al_2O_3) + (0.7)(\%\ Fe_2O_3)}{\%\ CaO + (1.4)(\%MgO)}$$

Quantitative thermal analysis

A more conclusive test for the hydraulic behavior of the mortar samples is obtained through the TGA. The weight loss corresponding to a specific temperature range provides information on the thermal transformations such as dehydration, dehydroxylation, oxidation, and decomposition. The TGA thermographs shown in Figures 4 and 5 record continuous weight loss for FA-1 and FA-2 from 22°C to 1000°C. The water absorbed was removed from the samples as the temperature reached 120°C. At a temperature of 120°C to 200°C, loss of hydrated salts accumulated through time and dehydration of gypsum are also eliminated (Cayme and Asor Jr 2016). Table 3 shows that FA-1 (3.80%) exhibited a higher weight loss until 120°C, compared to FA-2 (0.26%), which means that FA-1 has absorbed more water than FA-2. A possible explanation for this observation is FA-1's location, which is situated near the ground and has soaked up more water over time. Within the temperature range of 120°C to 200°C, both samples roughly have a similar weight loss pattern at less than 1.0%.

Sample	Weight loss (%)					
	< 120°C	120°C -200°C	200°C -600°C	> 600°C	Total Weight Loss	CO_2/H_2O
FA-1	3.80	0.84	11.97	12.73	29.34	1.06
FA-2	0.26	0.78	5.56	28.63	35.23	5.15

Table 3 Weight loss of FA-1 and FA-2 for every temperature range.

Structurally bound water on the surface of hydraulic mineral phases such as calcium-aluminum-silicate-hydrates or calcium-silicate-hydrates evaporates between the range of 200°C to 600°C. Impurities from organic compounds are also combusted at this temperature range (Ingo et al. 2004). The loss of weight of FA-1 is almost twice that of FA-2 and is evident from the TGA thermograph in Figure 4, showing a significant weight loss centered at 295°C. This observation is supported by the EDXRF data (Table 2), where it is observed that FA-1 has a higher LOI value, and the ratio of calcium and silicate is also more significant compared to FA-2. Thus, it can be assumed that FA-1 has more hydraulic clay minerals where the water can attach, and organic contaminants are more present due to the unaccounted LOI values, which can come from carbon compounds. A considerable drop in the mortar's mass happened within the range of 600°C to 850°C, attributed to the decomposition of $CaCO_3$. These patterns are characteristic of lime as the CO_2 is removed and typically originates from a recarbonated mortar (Moropoulou et al. 1995b). The maximum weight loss of FA-1 occurred earlier at 680°C, while for FA-2 at 793°C. The early decomposition experience by FA-1 is due to the dehydroxylated clay mineral illite present in the mortar during the calcination of lime. These dehydroxylated clays are responsible for providing strength to the mortar (Moropoulou et al. 1995a).

Furthermore, the CO_2/H_2O ratio from the thermograph is useful for classifying the extent of the binder's hydraulic nature. The ratio corresponds to the weight loss greater than 600°C (i.e., CO_2) and the temperature between 200°C to 600°C (i.e., hydraulic H_2O) (Moropoulou et al. 1998). The computed CO_2/H_2O ratio is seen in Table 3, where FA-1 is 1.06, and 5.15 for FA-2. Since these ratios are less than 6.0, both are classified under the hydraulic lime mortars group. The typical weight loss patterns further affirm this assumption for the hydraulic H_2O, which should be above 3.5%, and a CO_2 value of below 30%, for hydraulic mortars (Maravelaki-Kalaitzaki et al. 2003; Moropoulou et al. 2005). FA-1 and FA-2 also met these conditions. FA-1 can be classified further under the subgroup pozzolanic and portlandite mortar due to CO_2 weight loss values between 10 to 20% and a CO_2/H_2O ratio value below 3.5 (Moropoulou et al. 2000). The pozzolanic property most likely came from clay as the binder is heated from 400°C to 600°C. It is not surprising that clay is part of the production process because the province of Lanao del Norte, specifically Bacolod, has a sandy-clayey soil type (Province of Lanao del Norte n.d.).

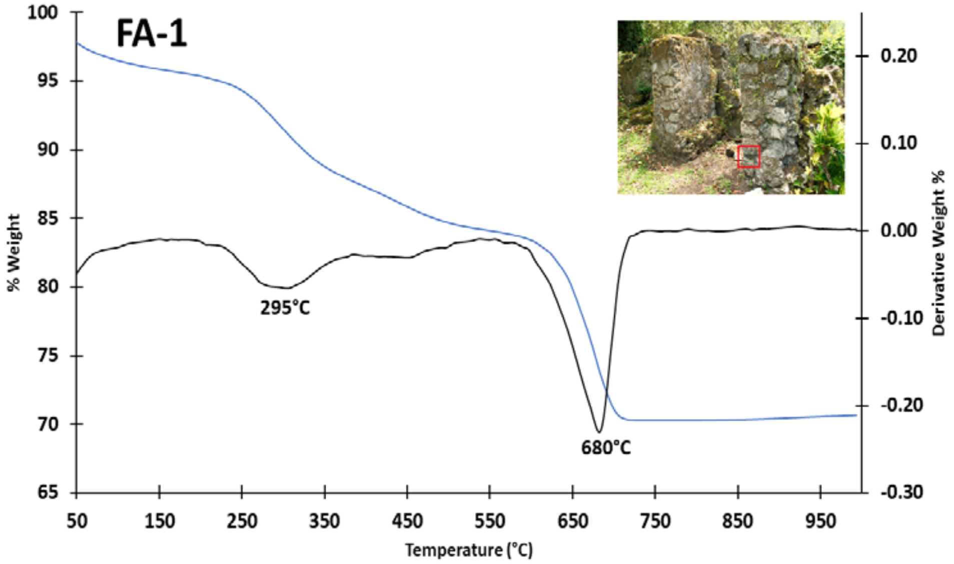

Fig. 4 TGA thermograph of FA-1 (blue line) including the 1st derivative plot (black line). Two significant weight losses were recorded, at 295°C and at 680°C (maximum).

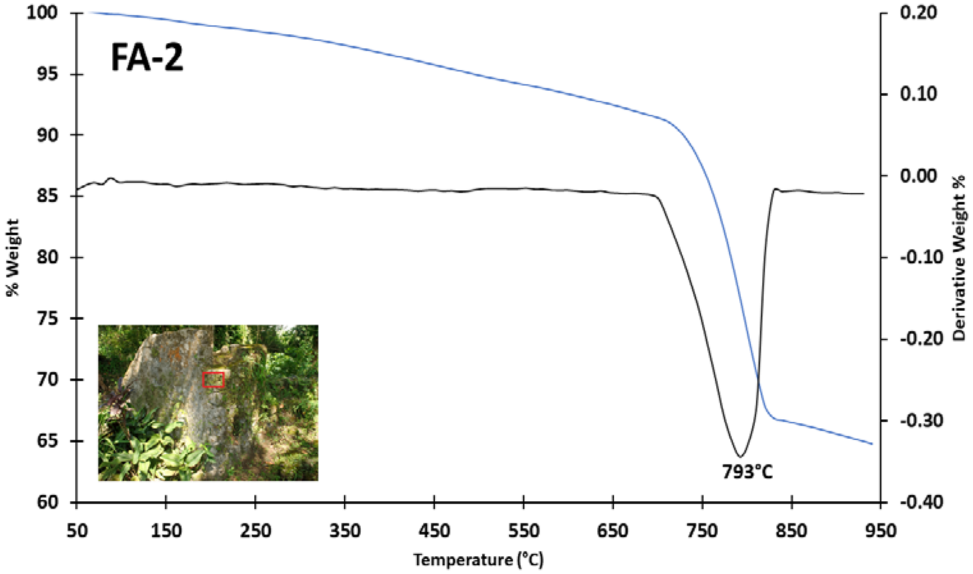

Fig. 5 TGA thermograph of FA-2 (blue line) including the 1st derivative plot (black line). Maximum weight loss was recorded at 793°C.

Conclusion

The combination of EDXRF and TGA techniques has provided a means to identify the hydraulic behavior of the mortar samples from Fort Almonte in Lanao del Norte. The quantity of major elements found in samples, FA-1 and FA-2, is typical of a mortar material made from lime, sand, and clay. Results show that pozzolans, most likely clay, are part of the lime binder mixture, imparting hydraulic nature to the mortars. FA-1 likely contains more clay than FA-2. These characteristics offer an advantage of faster setting time, considering that Fort Almonte is a defensive structure. Seashells are also presumed to be utilized for the lime raw material, and that open firing technique using stacks of wood may have been employed for calcination due to organic compound contaminations. The raw materials used to manufacture the mortars were likely sourced within the surrounding region.

For future studies, the sampling size should be increased, and different areas of the fort should be sampled to reflect the variability in the chemical and mineralogical composition. Fortifications or other structures built within the Spanish Colonial Period should be compared to the results of this study to determine the trends in manufacturing mortars. The possible source of lime and clayey soil should also be investigated for its composition and correlated with the mortar material. Furthermore, analytical tests such as X-ray diffraction (XRD) and inductively coupled plasma mass spectrometry (ICP-MS) should be utilized to validate the results of this study. Lastly, this paper has enlightened the construction process during the Spanish Colonial Period in the Philippines. It can encourage further scientific research on the chemistry of historical lime mortars both locally and in the Southeast Asia region.

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