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Application of thermal analysis in preservation and restoration of historic masonry materials

Part A. Characterization of materials

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Abstract Thermal analysis techniques have been used in characterizing building materials from significant historic properties in the Charleston, South Carolina area. Determining the chemical and physical effects of deterioration resulting from long periods of exposure is a first step in formulating preservation strategies. In this regard, simultaneous thermal analysis coupled with evolved gas analysis has been used to study reactions between air, seawater, and masonry materials. Further, the traditional petrographic identification of mortar composition is greatly facilitated through use of thermal analysis. Simultaneous thermal analysis allows for an exact determination of the calcium carbonate content in mortars as an alternative to the use of an inferred value based on chemical analysis data. The partial dissolution of calcium carbonate in the presence of sea salt is a major deterioration process. Further, natural cements manufactured in the United States are identified, in part, based on their thermogravimetric (TG) traces and their evolved gases. The data indicates that natural cements form some carbonate phases in addition to the major hydrate phases. Clay bricks are found to exhibit interaction with sea water, with uptake of bicarbonate suggested. Additionally, there is evidence of re-hydroxylation in the 160 year old bricks. The bricks made in coastal zones contain a considerable free silica fraction that is composed of a small percentage of cristobalite. The silica content of the clay bricks is seen to result in very high thermal expansion coefficients in the area of 10×10^{-6} to 12×10^{-6} K^{-1}. These studies provide guidance in restoration efforts where authenticity of cements is important. In the event that replacement bricks are required, matching the thermal expansion coefficient of the original bricks is a requirement for preservation of the masonry structure.

Keywords Historic masonry · Thermal analysis · Preservation · Restoration

Introduction

Characterization of masonry materials from historic structures typically involves petrographic analysis [1, 2]. In the standard method for analysis of hardened masonry mortar, a combination of petrography and chemical analysis is prescribed, except for cases in which magnesium hydroxide is found by petrography or X-ray diffraction [3]. In the latter case, differential thermal analysis (DTA) or thermogravimetric (TG) analysis is used to quantify the amount of magnesium hydroxide so that the dolomitic lime content of the mortar can be calculated. This can be misleading in the event that natural cements have been used since these cements contain magnesium. In addition, there is no standard method for examination of historic bricks, although damage in historic clay masonry is well known [4].

The identification of cements and quantification of lime contents in mortars are particularly challenging, and considerable experience is required in petrographic methods [2]. However, thermal analysis techniques provide an aid in the analysis to the extent that calcium carbonate is exactly determined [5]. The use of thermal analysis in addition to X-ray diffraction (XRD), and X-ray fluorescence (XRF) can greatly enhance petrographic analysis [5–7]. Characterization of historic clay bricks is essential for

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preservation and restoration processes [8]. Replacement materials must exhibit thermomechanical properties similar to the majority of bricks in the structure to prevent loss of the masonry bond in bricks resulting from differences in properties.

Examples are provided from historic building in the Charleston, South Carolina, area. These materials were studied as part of a preservation and restoration project for Fort Sumter National Monument supported by the National Park Service.

Experimental

Simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements were carried out on a Netzsch STA 449C which was coupled to a Brucker Vector 22 Fourier Transform Infrared Spectrometer (FTIR) for evolved gas analysis (EGA). The details of the coupling of the thermal analyzer and the evolved gas analyzer have been described by Kaiserberger and Post [9]. Simultaneous thermogravimetric (TG), differential scanning calorimeter (DSC), and evolved gas analysis (FTIR) measurements were obtained at a heating rate of 10 °C min^{-1}. A flow rate of 100 mL min^{-1} of simulated air (20% O_2 in N_2) was used for all experiments. Open crucibles were used in these measurements. The sample size ranged was 50 ± 2.5 mg. The differential scanning calorimetry (DSC) sensitivity curve was determined using a sapphire disk.

In this study, a resolution of 4 cm^{-1} was used for all FTIR measurements. The CO_2 and H_2O emission traces were determined by integrating the FTIR absorption spectra from 2,450 to 2,200 cm^{-1} for CO_2 and 2,200 to 1,600 cm^{-1} for H_2O. The evolved gas data was used to aid in the interpretation of the thermogravimetric (TG) and differential scanning calorimetery (DSC) data.

The thermal expansion of selected samples was measured with a Netzsch Dil 402 C Dilatometer using an alumina pushrod and sample holder. A heating rate of 5 °C min^{-1} was used for all measurements. The instrument was calibrated with an alumina reference standard. The X-ray powder diffraction (XRD) data was collected using a Scintag PAD-V diffractometer. Data was collected in a stepwise fashion from 5 to 65° 2θ with a step size of 0.02° 2θ. Data was collected for 4 s. at each step. Jade software was used to analyze the diffraction data. The X-ray floursecence (XRF) data was collected on a Thermo-Noran Quan-X EC energy dispersive X-Ray Fluorescence unit. The instrument was calibrated using a number of NIST Standard Reference Materials. The measurement of soluble salts was accomplished using ion chromatography. To determine the soluble salt content, samples were leached for 24 h in deionized water and the soluble salt content in the leachate was measured using ion chromatography (Dionex IC-2000). The pore size distribution was measured by mercury intrusion porosimetry using a Quantachrome Pore Master 33.

Mortar

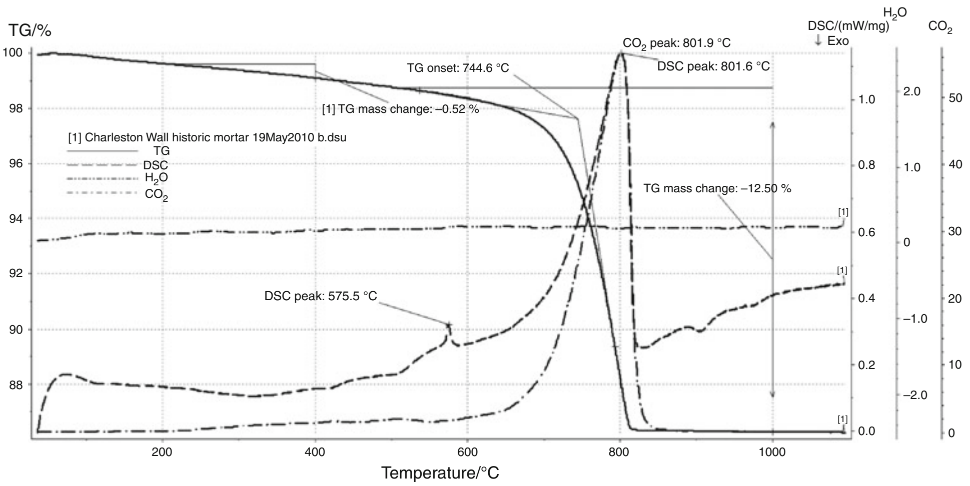
Masonry mortar composition evolved in the Colonial Period from use of burnt limes to use of manufactured cementitious materials. The earliest burnt limes were based on the abundant oyster shells found at the coast. This lime was hydrated by mixing it with water and aged until it was deemed sufficiently “tempered” for use, with the resulting mixture referred to as lime putty. The mortar was produced using a mixture of approximately one part of hydrated lime putty (binder) to 2–3 parts of sand by volume. After construction, the lime attained a rigid condition by absorption of carbon dioxide from the atmosphere forming calcium carbonate in situ.

A series of masonry fortifications were built around the City of Charleston during the colonial period for defensive purposes. Samples of the mortar were characterized to complement further preservation and restoration efforts for early period structures [8]. The thermal analysis of a sample of the original Charleston City Wall mortar is shown in Fig. 1. The mortar is comprised of calcium carbonate and silica sand, based, respectively, on observation of the decomposition of the carbonate (801.9 °C) and the alpha to beta quartz inversion (575.5 °C). The mass loss on carbonate decomposition of 12.5% implies a lime putty or $Ca(OH)_2$ content in the mortar of 21.0% by weight (dry basis). This equates to volumetric proportions of lime to sand of about 1:1.9.

X-ray fluorescence (XRF) analysis revealed that the mortar contained 14.39% by weight of CaO and 69.74% of SiO_2, while the insoluble residue (sand) exhibited slightly over 90% SiO_2. The bulk density of the mortar was 1.70 g/cm^3 and the apparent porosity was 25.9%, with a percentage of <1 μ pores of 45.86% (by mercury intrusion porosimetry). The pore fraction <1 μ suggests that the mortar was not substantially corroded; although the material had a noticeable sulfur smell and exhibited soluble sulfate on water extraction using detection by ion chromatography. The soluble salts were likely from exposure to sea water or from the absorption of ground water into the pores of the brick. During subsequent drying phases, the soluble material was deposited in the pores of the brick [10].

The specimen from the Charleston wall was considered as “typical” of a lime based mortar from the Colonial Period. Similar results were observed in subsequent

Fig. 1 Thermal analysis of mortar from historic Charleston (SC) wall circa 1713



analysis of mortar specimens from other structures built prior to the availability of manufactured natural cement (~1840).

A specimen of lime based infill material from Fort Sumter National Monument was subjected to thermal analysis, as shown in Fig. 2. The use of infill between interior and exterior walls allowed for cost savings over through-wall masonry construction. There are distinct differences, however, in the thermal analyses of the infill material and the lime putty mortar used in the Charleston wall.

The infill material exhibits a distinct carbonate decomposition peak at 760 °C; however, the peak at 661 °C suggests the presence of magnesium carbonate [7]. Further, the water evolution at 351 °C is in an area where cement dehydration is expected. The expected quartz inversion peak confirms the presence of silica sand. Petrography was required to further characterize the mortar (Fig. 3).

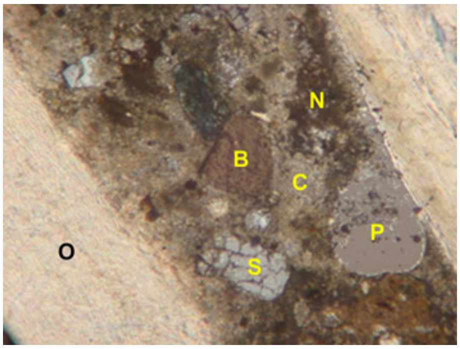
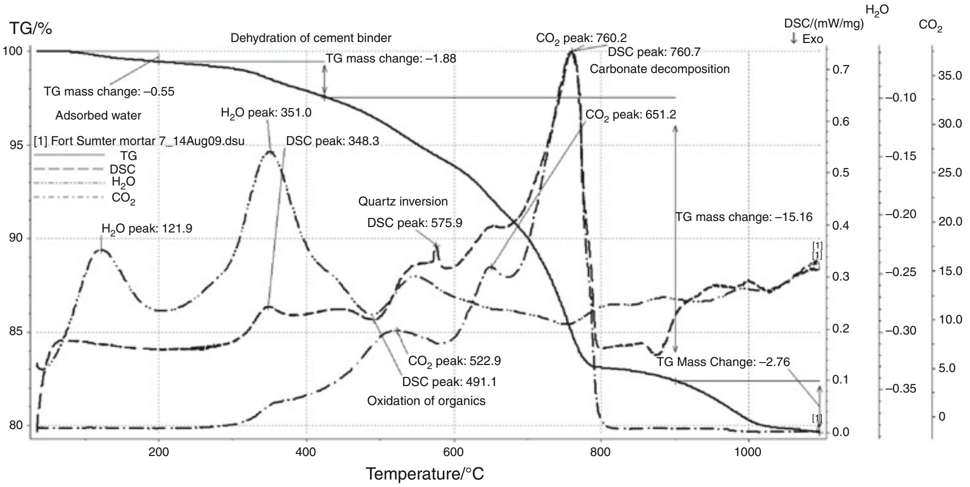


Fig. 3 Polarized light microscopy of infill rubble/tabby mortar

The microscopy identified a brick fragment (B), oyster shells (O), silica sand (S), a pore (P), in a matrix or continuum of calcium carbonate (C). Some natural cement (N) is present explaining the cement dehydration shown in Fig. 2. Historic records show that “Rosendale Cement”, a burned argillaceous dolomitic limestone, was used in the majority of the construction of Fort Sumter. It appears that the infill was composed of any type of solid substance that was at hand during construction. The infill material exhibited a density of 1.85 g/cm^3 and a porosity of 20.8%. The percentage of porosity <1 μ was 56.6% suggesting

Fig. 2 Thermal analysis of infill rubble with tabby mortar, Fort Sumter National Monument, circa 1850



that the infill exhibits significant capillary suction and retention of water.

According to historic records, Rosendale natural cement based mortar was used in construction of the Fort Sumter walls. The thermal analysis of a mortar from Casemate A18 in the Fort Sumter National Monument, an area of original construction not destroyed in any of the bombardments of the Fort is shown in Fig. 4. The thermal analysis results suggest the presence of a natural cement such as Rosendale [11, 12]. The evolved gas analysis (EGA) traces for H_2O and CO_2 evolutions in the general range of 250–400 °C are due to decomposition of cementitious phases with an accompanying mass loss of 1.55%, and such dehydrations are expected when Rosendale cement was a mortar constituent [11]. Likewise, the increasing CO_2 evolutions above 400 °C are seen in Rosendale/natural cement mortars, as a multiplicity of carbonate species decompose on heating.

The twin CO_2 evolutions at 654.6 and 734.0 °C that were observed in the thermal analysis of the mortar from Fort Sumter Casemate A18 suggest that the mortar contained dolomitic limestone [7]. The presence of dolomitic limestone was confirmed by X-ray diffraction as shown in Fig. 5. While dolomitic limestone relics can be found in residual natural cement particles in the mortar, some materials at the Fort were found to contain a distinct addition of dolomitic limestone. It appears that the dolomitic limestone admixtures produced white colored

Fig. 4 Thermal analysis of Fort Sumter National Monument, casemate A18 mortar circa 1850

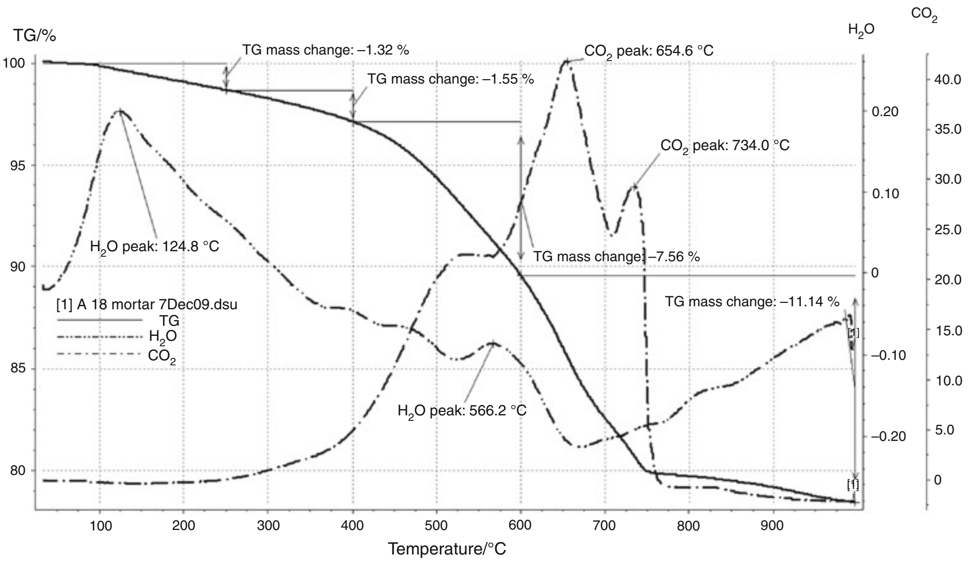
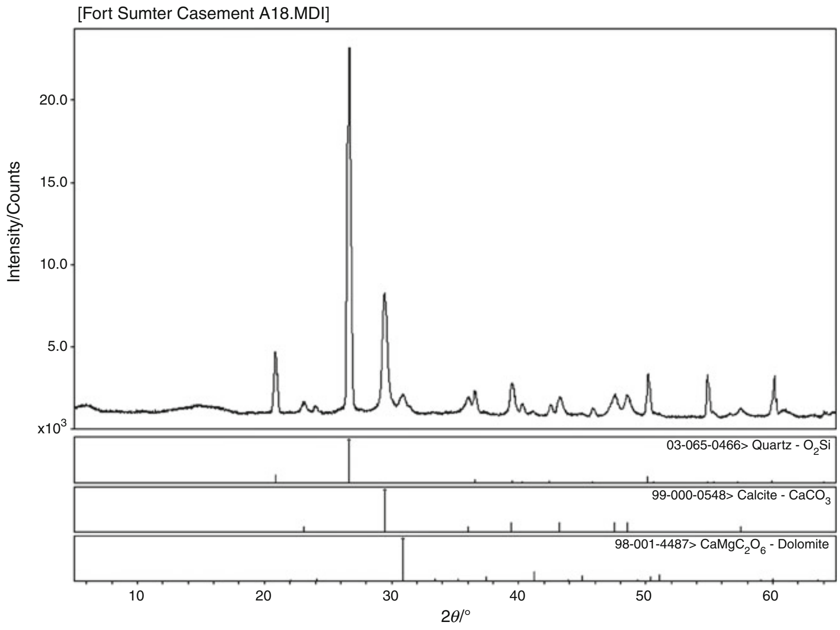


Fig. 5 X-ray diffraction analysis of Fort Sumter National Monument, casemate A18 mortar circa 1850



mortars or coatings. A white color was apparently required in the casemates due to poor lighting in these areas.

The microscopy of the mortar from Fort Sumter Casemate A18 is shown in Fig. 6 where a Rosendale cement relic (C) is positioned in the matrix (M) of cement and carbonated lime. Walsh has shown that cement relics can be viewed in the microstructure of historic mortars, inferring causes originating in poor grinding of early natural cements and in hand mixing of mortars [2]. The sand (S) from coastal areas was contaminated with iron pyrite (Py). The pore (P) exhibits a carbonate rim, a consequence of soluble calcium being present and the ageing of the mortar.

This mortar specimen exhibited a composition of 18.14% CaO, 44.50% SiO_2, and 1.22% Fe_2O_3. The bulk density of 2.00 g/cm^3 was surprisingly high (apparent porosity of 11.92% and percentage of <1 μ pores at 65.31%). The mortar was found to contain a significant amount of soluble chloride and sulfate by ion chromatography, and scanning electron microscopy results suggested corrosion of the natural cement relics in the microstructure. The soluble salts likely originated from infiltration of seawater into the pores of the masonry [10]. The low porosity of the mortar may be due to infiltration of the masonry by calcium laden water from above the uncovered and now Portland cement-capped casemate, with subsequent deposition of calcium salts in the pores of the mortar [10].

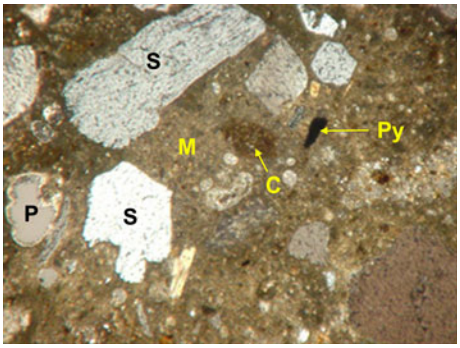


Fig. 6 Polarized light microscopy of Fort Sumter casemate A18 mortar (XPL)

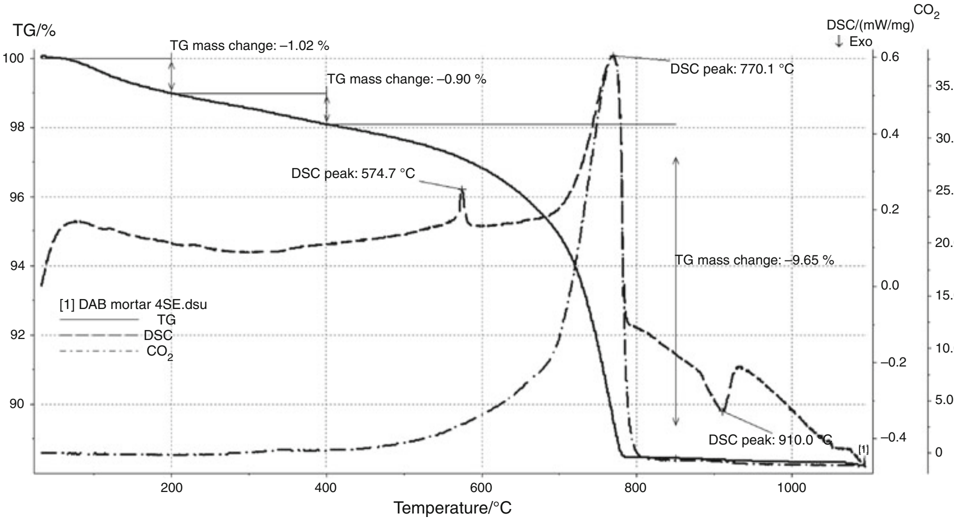
The thermal analysis from a Portland cement based mortar from a 1950-era seaside building is shown in Fig. 7. The mortar was identified as Type-O masonry mortar (volumetric proportions of 1 part Portland cement, 2 parts hydrated lime and 9 parts sand) [3]. The thermal analysis shows a weight loss of 0.9% in the cement dehydration region of 200–400 °C, the alpha to beta quartz inversion at 574.7 °C, and the calcium carbonate decomposition at 770.1 °C. The exothermic reaction at 910 °C is likely related to the interfacial reaction between lime and sand on heating forming anorthite or $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ [13, 14].

The microstructure of the mortar from the 1950's building is shown in Fig. 8. The matrix (M) in the machine-mixed mortar is a uniform composition of cement hydrates and carbonated lime surrounding sand grains (S) and containing porosity (P). The mortar analysis by XRF exhibited 15.19% CaO, 78.76% SiO_2, 0.60% Fe_2O_3, and 0.37% S. The mortar bulk density was 1.93 g/cm^3 with an apparent porosity of 21.13% and a percentage of pores <1 μ of 68.98%. This high percentage of pores <1 μ may be the result, in part, of salt related corrosion due to sea spray impingement on the structure. Lubelli has delineated the mechanism of corrosion of mortar constituents by salt [10].

Brick

The application of thermal analysis in characterization of historic clay bricks is illustrated by the thermal analysis

Fig. 7 Thermal analysis of Portland cement mortar, circa 1950



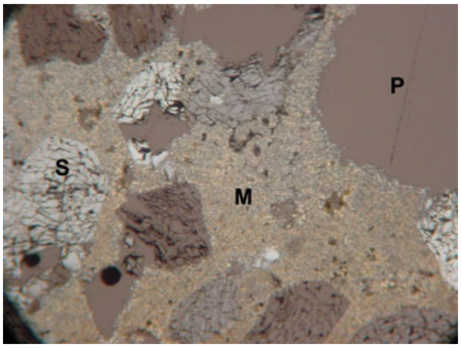


Fig. 8 Polarized light microscopy of the 1950's Portland cement based mortar (XPL)

trace of an upper gorge wall brick from Ft. Sumter National Monument, as shown in Fig. 9. An interesting CO_2 evolution is seen on heating with a peak at 364.2 °C suggesting the presence of iowaite as a reaction product between sea water and the vitrified clay, as iowaite is known to decompose step-wise above 266 °C with a characteristic CO_2 evolution in the area of 523 °C [15]. In this case the combination of traditional thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) with evolved gas analysis (EGA) allows for the identification of minerals that are difficult to detect by other means. The continuing H_2O evolution above 500 °C suggests re-hydroxylation of the clay constituent of the bricks [16].

The chemical analysis of the brick was 10.56% Al_2O_3, 80.41% SiO_2, 0.59% CaO, and 4.00% Fe_2O_3. The brick bulk density was 1.57 g/cm^3 with an apparent porosity of 36.8%. This data is consistent with hand-molded bricks made from coastal marl. The bricks exhibited significant water soluble sodium and chloride suggesting infiltration of seawater into the pores of the brick [10].

The thermal expansion of the bricks shows a low temperature expansion above 110 °C in the area expected for the alpha to beta cristobalite inversion, as shown in Fig. 10. The expansion coefficients of 12.9×10^{-6} to 13.5×10^{-6} K^{-1} reflect the significant content of free silica in the composition, and similar values are also seen in fired silica refractory bricks. Since vitrified clay bricks made from clay

Fig. 9 Thermal analysis of a brick from Fort Sumter National Monument, upper gorge wall, reconstruction of 1896

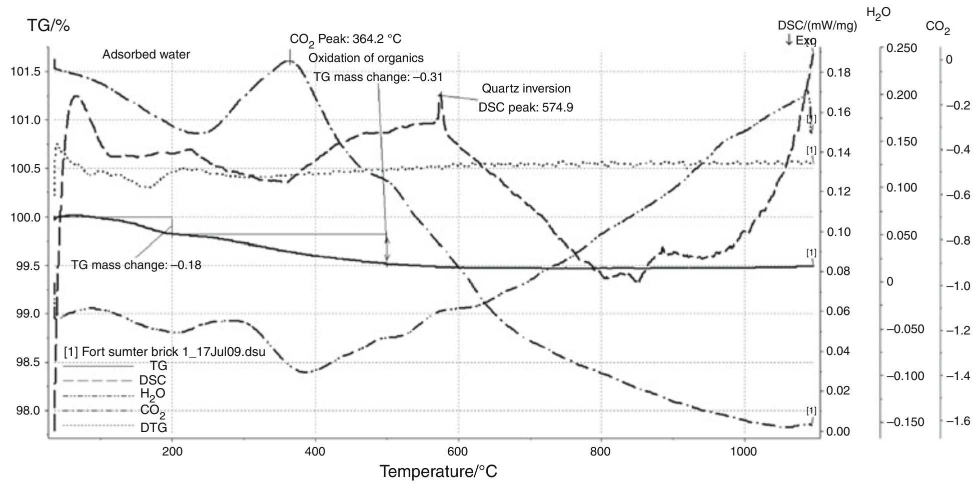
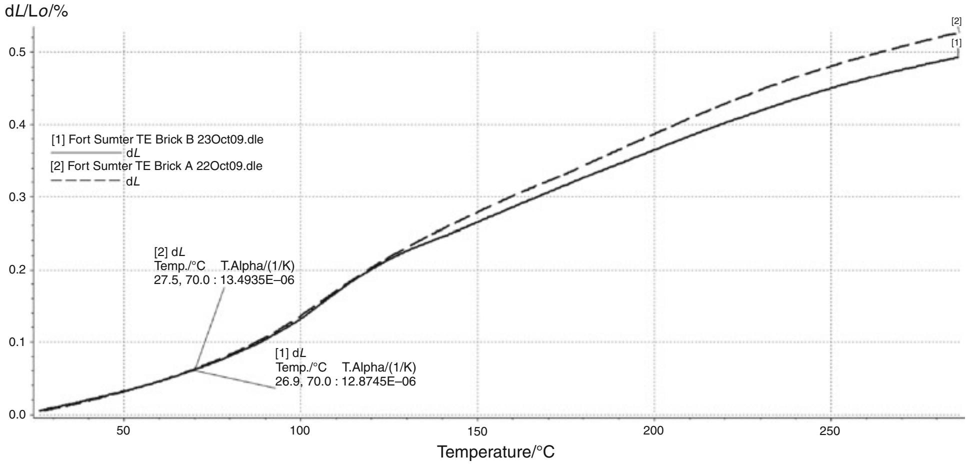


Fig. 10 Typical thermal expansion data for 1850's brick based on coastal marl



or shale typically exhibit expansion coefficients of 4×10^{-6} to 8×10^{-6} K^{-1}, there are important implications on replacement brick selections for restoration in historic coastal buildings. Use of lower expansion bricks in replacement wall sections for structures containing higher expansion bricks can lead to loss of masonry bond and loosening of bricks in the replacement sections over time.

Summary

Thermal analysis methods were used in characterization of masonry mortars and bricks. Simultaneous thermal analysis and evolved gas analysis provided distinctive results for lime based mortar, mortars containing natural cement, and mortar containing Portland cement. Thermogravimetric analysis provides a method of accurately determining the amount of hydrated lime in the original mortar mix based on the observation of the calcium carbonate decomposition. The determination of the lime content of the mortar by thermal analysis is likely more precise than use of inferred methods based on chemical analysis.

The thermal analysis of historic bricks showed the possible presence of reaction phases between sea water and the bricks. Further, the water evolution on heating suggests that the bricks experienced re-hydroxylation in 160 years of environmental exposure.

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