Construction and Building Materials 149 (2017) 139–148

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Characterization of the superficial weathering of bricks on the City Wall of Xi'an, China

Pu-jun Jin [a,*], Yue Zhang [a], Su Wang [b], Xiao-gang Yang [c], Maolin Zhang [d]

[a] School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710069, PR China
[b] Xi'an HanGuangmen Museum, Xi'an 710054, PR China
[c] Chongqing Cultural Heritage Research Institute, Chongqing 410013, PR China
[d] Jingdezhen Ceramic Institute, Jingdezhen 333001, PR China

HIGHLIGHTS

- Efflorescence, exfoliation and pelletizing were classified as main deteriorations.
- Calcium-containing salts are detected as main component in efflorescence.
- The similar material composition was identified in the exfoliation and pelletizing samples.
- The high content of S and N were detected in the exfoliation and pelletizing samples.

ARTICLE INFO

Article history:
Received 29 October 2016
Received in revised form 23 April 2017
Accepted 6 May 2017

Keywords:
Heritage
Masonry construction
Bricks
Efflorescence
Exfoliation
Pelletizing

ABSTRACT

This study characterized the influence of salts on bricks in correlation with the efflorescence, exfoliation and pelletizing occurring in the ancient brick wall at Xi'an, China. After 640 years of atmospheric exposure, many bricks have suffered from efflorescence, exfoliation and pelletizing. Different scientific instruments, such as optical microscopy (OM), X-ray fluorescence analysis (XRF), X-ray diffraction (XRD), thermal analysis (TGA/DTG) and X-ray photoelectron spectroscopy (XPS), have been applied to investigate the chemical and mineralogical components of the salty crusts and evaluate their species and accumulative quantities. The results show that the detected salts are chiefly aggressive deterioration problems that are causing serious damage to the brickwork. Calcium-containing salts with a dominant amount of calcite ($CaCO_3$) and ~2.3 at.% of gypsum ($CaSO_4{\cdot}2H_2O$) were detected as the main components in the efflorescence sample, demonstrating the significantly large amount of efflorescence that occurs on shining days after rainy days. This results from the almost insoluble $CaCO_3$ that occurs via a neutralization reaction of calcium hydroxide [$Ca(OH)_2$] that migrates from the puddled clay core and carbon acids on the surface of the bricks. The flaking and powdering of bricks demonstrate different weathered morphologies that have similar material compositions that are classed as exfoliation and pelletizing and are responsible for the presence of some salty ions, such as C, S and N, due to halite (NaCl), thenardite (Na_2SO_4) and metal nitrates [$M(NO_3)n$] at a total of 10 at.%. With a comprehensive cognitive objective, this research contributes to a new understanding of weathered phenomena that occur on the surface of bricks in brick-clay structures without neglecting the effective removal of salty ions that regularly accumulate on the surface of porous fictile structures.

1. Introduction

As a famous architecture, the Xi'an City Wall was built as a fortification to defend ancient Xi'an, representing one of the oldest, largest and best preserved Chinese city walls. After the first emperor, Zhu Yuanzhang, of the Ming Dynasty (1368–1644 CE) unified the entire country, he began to enlarge the Xi'an City Wall that was previously constructed in the Sui and Tang Dynasty (581–907 CE). This 'big build' project started in 1370 CE and was completed in 1378 CE as a military defence system with an important update that embraced the puddled clay core by using huge bricks that were approximately 45.0 cm wide, 22.5 cm long and 9.5–10.0 cm high. After its extension, the wall now stands at a height

* Corresponding author.
E-mail address: jinpj@snnu.edu.cn (P.-j. Jin).

http://dx.doi.org/10.1016/j.conbuildmat.2017.05.045
0950-0618/

of 12 m, 12–14 m wide at the top and 15–18 m thick at the bottom, covering 13.7 km in length and surrounded by a deep moat, as shown in Fig. 1a and b. Sectional remains excavated at the Hanguangmen Site in 2004 demonstrated a clay-brick structure, as shown in Fig. 1c.

The porous building materials, including brick and stone, easily suffer from damage from various salts that originate from various sources, primarily due to soluble salt crystallization cycles [1]. In most cases, some of the primary sources of salt contamination include a capillary flow of saline groundwater, surface water and moisture from the surrounding atmosphere or absorption of salt-laden precipitation and aerosol pollutants [2–3]. Salts may originate from the brick itself, such as S- and Ca-rich zoning detected in fired clay brick [4], or they may originate from the mortar, such as lime-based mortars and cement-based mortars [5–6]. There is great variety in the types of salts encountered and marked differences between different regions [7].

Xi'an City Wall differs significantly in many weathered aspects from the masonry construction and earthen architecture. The puddled clay core has resulted in huge and abundant cracks on its surface and the occasional collapse of its partial area. Specifically, the moisture from the puddled clay core is considered to play a key role in prompting the migration of soluble salt from the puddled clay core to the surface of the wall bricks [8–10]. Therefore, large whitening areas [11] are frequently seen on the middle parts of the city wall that accompany the serious damage on the brick surface [12,13], and this has become a major source of mechanical damage to the brick structure [14].

The crystalline salts that cause efflorescence have been reported to be NaCl, $NaNO_3$, $Na_2SO_4{\cdot}10H_2O$ and Na_2SO_4, and it is due to groundwater and rainfall [15,16] and derived from their key physical and chemical parameters, such as porosity and specific surface area, mineralogical analysis, total chemical content and soluble salts. Although numerous studies have been performed to elucidate the causes of efflorescence, it is such a complex phenomenon that it is still a permanent problem [17].

In our view, three main weathered morphologies can be observed on the surface of the bricks on the Xi'an City Wall that correspond to salts. These have been classified as efflorescence, exfoliation and pelletizing, as shown in Fig. 1. In this study, multiple analytical methods were applied to reveal the influence of the salts in correlation to the efflorescence, exfoliation and pelletizing on the surface of the bricks.

2. Samples and instruments

2.1. Samples

Many of the original bricks used in the Xian' City Wall were largely replaced with new bricks during repairs from the Qing Dynasty to the present. Our work focuses on the various corrosive morphologies that have occurred on the surface of the original bricks. The white salty crust (classified as efflorescence, as shown in Fig. 2a and b) can cause large whitening areas after the alternation of wet and dry days on the surface of its middle parts, which is seldom observed in the lower parts of the original bricks but is obviously observed on the surface of replaced bricks.

The superficial cracking phenomenon (classified as exfoliation) can lead a serious damage to the original bricks, which has occurred not only in large areas but also in some isolated bricks, as shown in Fig. 2c and d. Many clay-like corrosive products (classified as pelletizing) appear on the surface of the original bricks, as shown in Fig. 2e and f. The pelletizing has caused a gentle erosive and gradual process on the superficial layer of bricks compared with exfoliation, which has caused drastic and deep damage.

On December 2, 2015, the white salty crust, cracking fragments and clay-like material were collected from bricks from the Xi'an City Wall near the Hanguang Gate for further research.

For the efflorescence sample, only white salty crust above the brick was carefully scraped away using a knife blade from the surface of the bricks without the substrate. The cracking fragments on the surface of the brick were removed using a tooth stick that was prepared for the exfoliation sample. The clay-like material collected using a knife blade has a loose structure, like chessom, and was used for the pelletizing analysis.

Considering the complicated weathered materials [18], to achieve reliable results, two parallel samples of approximately six pieces of weathered samples that had the same damage but were from different areas were studied, as shown in Fig. 3.

2.2. Instruments

The powdered weathered materials were analysed using XRD via a Rigaku Smart lab X-ray diffractometer equipped with Cu Kα radiation and recorded in the 2θ range from 5° to 80° with a tube voltage of approximately 40 kV and a current of approximately 30 mA. A Shimadzu XRF-1800 fluorescence spectrometer (XRF)

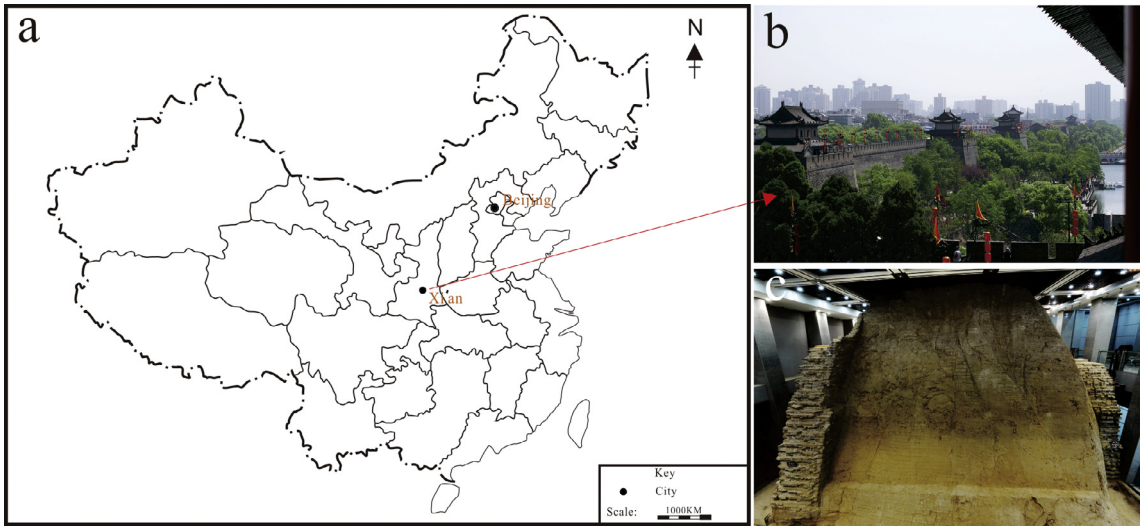

Fig. 1. The location of the Xi'an City Wall in China (a), a picture of one of its corners (b) and its cross-section at the Hanguangmen Site (c).