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Historical and Physicochemical Analysis of the Clinker Bricks in the Smart Memorial Gymnasium of the Tiancizhuang Campus at Soochow University, China

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Abstract: Clinker bricks were popular as a facade material in the United States between the 1890s and the 1930s. However, this material was unknown to Chinese builders and was seldom found in Chinese modern architecture from 1840 to 1949. The Smart Memorial Gymnasium built in the years 1934–1937 in the Tiancizhuang Campus of Soochow University (Suzhou, China) is one of the rare examples of a building featuring clinker bricks in modern China. Notably, those clinker bricks were not imported but locally manufactured. Despite the heritage significance of the Smart Memorial Gymnasium as part of a major historical and cultural site protected at the national level in China, the history and characteristics of those historical bricks have remained virtually unexplored. This study first provides a historical analysis of those bricks, giving insights into the general knowledge of this construction material around that time based on British and American historical sources from the 19th and 20th centuries, with a focus on historical treaties and documents. This analysis sheds light on the raw materials mixtures of clinker bricks, their manufacturing processes, and their architectural applications at the time. Moreover, this study presents a physicochemical analysis of the clinker bricks employed at Soochow University, focusing on the correlation between historical studies and physicochemical characteristics, as well as the materials' characteristics that respond to the natural environment. X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), and total immersion tests were employed to investigate the physicochemical properties of the bricks at various locations of the Smart Memorial Gymnasium facades. Our findings deepen the knowledge and understanding of clinker bricks transferred from the West to China in the early 20th century. Additionally, our results reveal the chemical composition and physical characteristics of different types of clinker bricks used in the Smart Memorial Gymnasium, outlining practical implications and future research directions. Overall, this study lays a foundation for the heritage recognition and conservation of Chinese clinker bricks.

Keywords: clinker bricks; historical analysis; chemical composition; water absorption coefficient; Smart Memorial Gymnasium

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1. Introduction

Overburnt bricks have a long history of being occasionally used as a decorative element in various parts of the world. However, it was only from around the 1890s that overburnt bricks—in the form of clinkers or clinker bricks—gradually became popularized as an expressionist architectural design language in the United States and beyond. The old term "clinkers" more commonly appeared in books and magazines in the Old World (e.g., Britain), while the new term "clinker bricks" became more widely used in the New World (e.g., USA). This terminological shift probably marked a transition in the understanding of this material. Clinkers were considered deformed waste material due to the poor control of the brickmaking processes, hence they were supposed to be discarded by the brick clamps or kilns. By contrast, clinker bricks were regarded as a new type of decorative brick, not necessarily worse than ordinary bricks, but with some “odd”, “quaint” decorative nature [1].

One of the challenges of using this material is its irregular shape, which leads to mortar joints with uneven thickness and potential cracking issues. A good example is the Colonia Güell Crypt (1908–1914) designed by Antoni Gaudí, which was built with clinker bricks. Gaudi’s intention was both decorative and structural. In this building, clinker bricks were intended to take on the load not only of the crypt itself but also of the church that should have been built atop it (although the church was ultimately never built). Another important Spanish figure in the application of clinker bricks is the Spanish architect and builder Rafael Guastavino (1842–1908), who played a significant role in exporting the “Tile Arch System” from Spain to the United States. Being patented in the United States in 1885, his system was used for constructing robust, self-supporting arches and architectural vaults using interlocking clinker bricks and mortar layers.

At the turn of the 20th century in the United States, the American architect A. C. Schweinfurth and the American architectural firm “Green & Greene” (Pasadena, CA, USA) [2,3] were among the early pioneers to explore the expressionist value of clinker bricks, which were associated with the local Arts and Crafts Movement. Subsequently, clinker bricks were promoted to a certain extent in the United States, especially in California and Oregon on the West Coast, in Illinois, Michigan, Pennsylvania, etc., in the Great Lakes region, and on the East Coast. In this process, the Common Brick Manufacturers’ Association of America (CBMA) played a pivotal role in promoting the “skintled brickwork”—which was widely used for clinker brick walls—by summarizing the brick lay methods quantitatively [4,5]. While the fashion of using clinker bricks continued in the United States into the late 1930s, the same trend had an impact on neighboring Canada and beyond, including faraway countries, such as China (Figure 1).

The local production of “foreign-style red bricks” in China had taken place since 1858 to supplement and gradually replace the Chinese native “blue bricks” first employed in early Western-style architecture. However, the use of clinker bricks for decorative purposes was unknown to Chinese builders and seldom found in Chinese Modern architecture in 1840–1949. A rare example of a building featuring clinker bricks in Modern China is the Smart Memorial Gymnasium (built 1934–1937) in the Tiancizhuang Campus of Soochow University (i.e., the University’s main campus, whose construction started in 1900) inside the walled city of Suzhou. Notably, the Smart Memorial Gymnasium was part of the last building project of the Soochow University main campus. Our increasing knowledge of the building history of the Tiancizhuang Campus has revealed the direct American influence in the use of clinker bricks of the Smart Memorial Gymnasium. According to University archives, Soochow University was established by the Methodist Episcopal Church, South (MECS) from the United States. A local brickyard called “The Soochow Brick & Tile Co.” was founded in 1921 in Suzhou by Dr. John A. Snell, a MECS missionary. Snell donated “$1000 worth of bricks” through the Soochow Brick & Tile Co. to the Smart Memorial Gymnasium when the University experienced financial hardship (United Board, RG011-271-4312: 7). Furthermore, the Smart Memorial Gymnasium was designed by the Shanghai-based architectural firm “Eastern Asia Architects & Engineers Corporation” (EAAEC), whose manager C. K. Chien had studied at the Rensselaer Polytechnic Institute (United States) around 1925, when clinker bricks were popular there. (Figure 2).

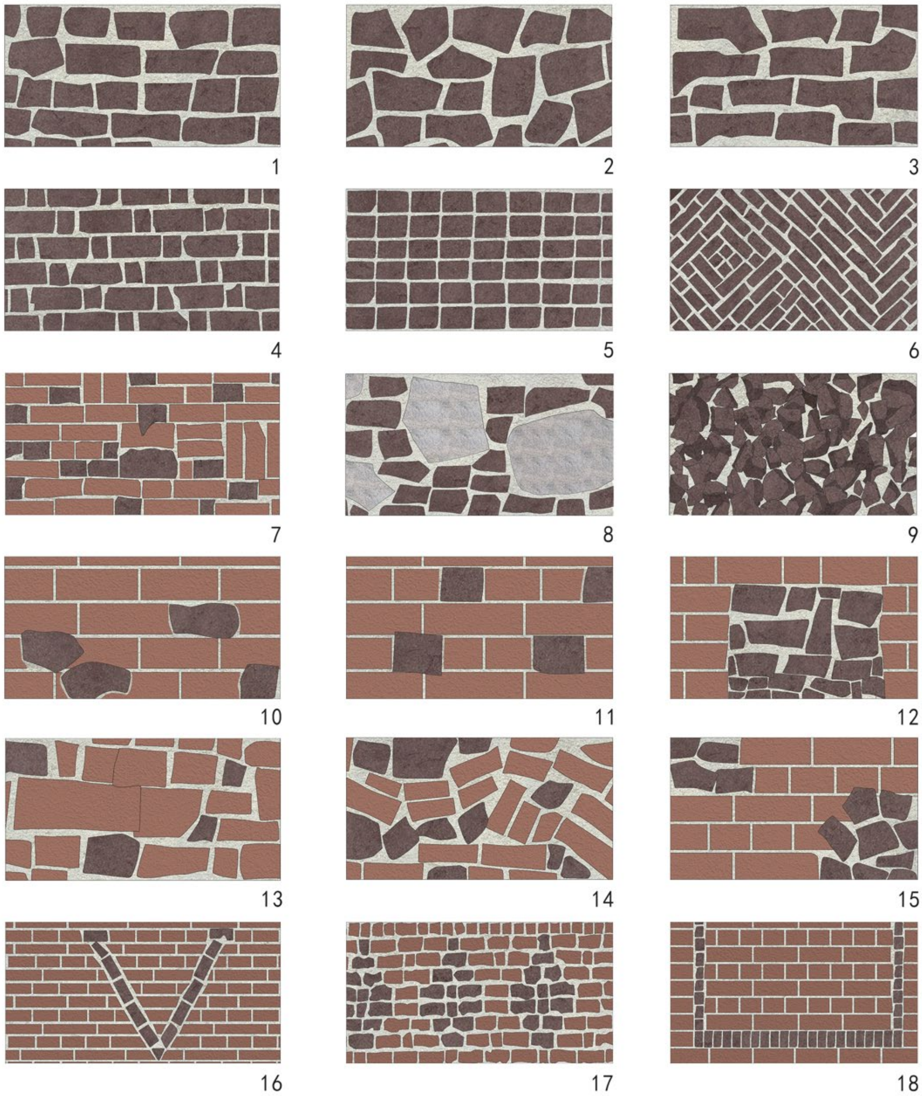


Figure 1. Diversity of clinker brickwork patterns and morphological clinker brick types based on examples worldwide (References: (1) 37 Penn Boulevard, Scarsdale, NY, USA, 1930. (2) Smart Memorial Gymnasium in the Tiancizhuang Campus of Soochow University, Suzhou, China, 1937. (3) William R. Thorsen House, Berkeley, CA, USA, 1909. (4) The Chateau Apartments, Queens, NY, USA, 1922. (5) Trinity Episcopal Church, Roslyn, NY, USA, 1906. (6) 7 Cohawney Road, Scarsdale, NY, USA, c. early 20th century. (7) The old zookeeper's house at Riverdale Farm, Toronto, Canada, 1902. (8) Gamble House, Pasadena, CA, USA, 1908–1909. (9) Smart Memorial Gymnasium in the Tiancizhuang Campus of Soochow University, Suzhou, China, 1937. (10) Holy Trinity Anglican Church, Edmonton, Canada, 1913. (11) Jan van Hoesen House, Claverack, NY, USA, 1730. (12) Holy Trinity Anglican Church, Edmonton, Canada, 1913. (13) Memorial Park Cemetery, Oklahoma City, OK, USA, 1927. (14) Memorial Park Cemetery, Oklahoma City, OK, USA, 1927. (15) Blessed Trinity R.C. Church, Buffalo, NY, USA, 1928. (16) Jan van Hoesen House, Claverack, NY, USA, 1730. (17) Decorative Clinker Brick Ornamentation on Parapet and Door Surround, 39–67 48th Street, Jefferson Court, Queens, NY, USA, c. early 20th century. (18) Decorative Clinker Brick Ornamentation on Facade, 39–79 to 39–8149th Street, Harrison Place, Queens, NY, USA, c. early 20th century.

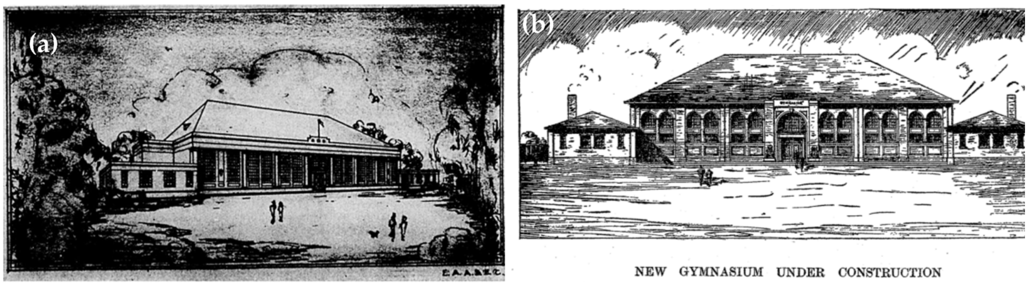


Figure 2. (**a**) Design drawing of the Gymnasium in 1929 (Source: Special Collections, Divinity Library, Yale University, United Board for Christian Higher Education in Asia, RG011-270-4309: 339.). (**b**) Design drawing of the Gymnasium in 1934 (Source: Special Collections, Divinity Library, Yale University, United Board for Christian Higher Education in Asia, Report of Soochow University to the China Conference, M.E.C.S., 1 November 1934.).

From aesthetic and cultural points of view, the application of clinker bricks in the last building project of the Soochow University campus (mid- and late 1930s) expressed the religious and aesthetic ideas prevalent in this Christian university at that time, as well as the environmental, economic, and social conditions of the locality. In 1927, China and its higher education system entered the nationalistic period, which made the identity of foreign-established Christian universities a particularly sensitive issue. As the free creation of architectural forms was restricted by the social atmosphere, materials became the most important expressionist language in the construction of the Soochow University campus. Given the frequent use of clinker bricks in local "quaint" English-style houses and Gothic Revival buildings in the United States in the 1920s and 1930s, their application in the Smart Memorial Gymnasium silently expressed the deep American connection of Soochow University (Figure 3).

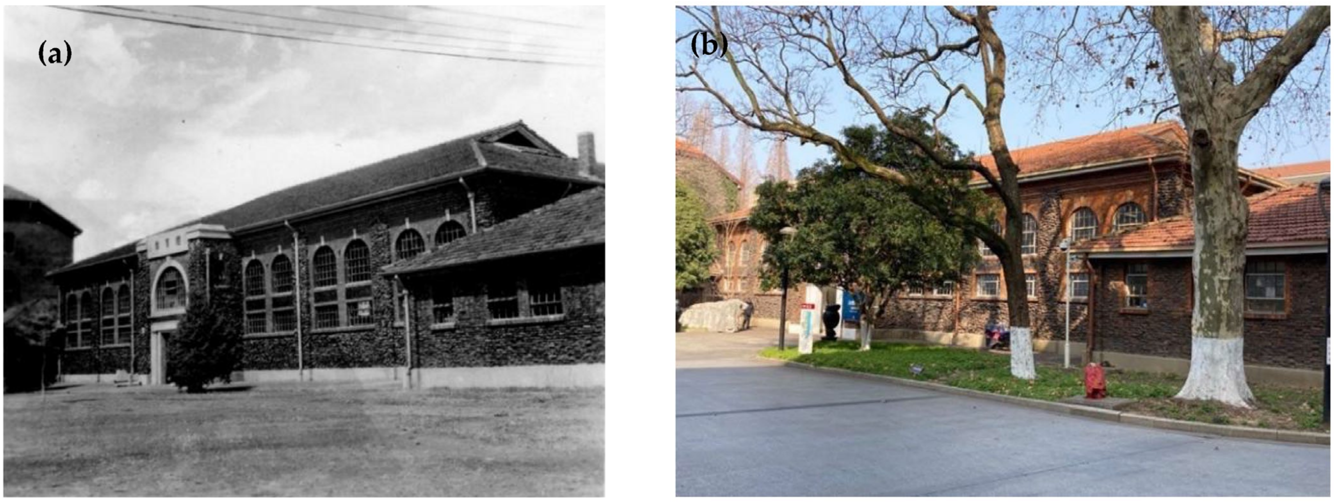


Figure 3. (**a**) Smart Memorial Gymnasium in the early 20th century (Source: Special Collections, Divinity Library, Yale University, United Board for Christian Higher Education in Asia, RG011-415-5874-5001), and (**b**) Smart Memorial Gymnasium in 2022.

To the best of our knowledge, very few studies have examined historical clinker bricks and specifically Chinese clinker bricks. Yost examined the design practice of the firm "Green & Greene" (Pasadena, CA, USA) in the United States, briefly touching on their pioneering creative use of clinker bricks since the beginning of the 1900s [3]. Akhtar provided the first systematic study of historical clinker bricks in the United States, with a focus on the aesthetic value and social-cultural histories of clinker bricks but without vigorously examining the technical aspects of clinker brick production. Moreover, Akhtar's thesis barely mentioned clinker brick examples outside the United States [6]. In a recent study about the development of the Tiancizhuang Campus of Soochow University, China, Pan and Chen touched on the use of clinker bricks in the Soochow University campus [7], but their paper did not investigate their material characteristics. Koleda and coworkers constructed a model representing the required ratios of the main oxides in the chemical composition of the ceramic to obtain clinker bricks with the prescribed properties at different firing temperatures [8]. However, their study focused on the fabrication of high-quality clinker bricks instead of historical clinker bricks. Levitskii and coworkers examined the raw materials and obtained data on the oxide and mineral composition to predict the composition of the charge for producing clinker bricks, the heat-treatment regimes, and the properties of the clinker bricks [9]. Although they provided comparative technical information, the study focused on regional poly-mineral raw material.

In recent years, a number of analytical techniques have been available for heritage science. The analytical techniques for masonry building can be divided into two different categories: (a) the in-situ non/minor destructive testing, including infrared thermography, moisture meter, Karsten/RELIM tube, portable syringe air permeameter, ultrasonic tomography, and resistance and compressive stress tests, such as flat jacks and hole drilling; (b) laboratory testing, including scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD), X-ray fluorescence (XRF), and Raman spectroscopy. These advanced analytical techniques enable a deep understanding of heritage materials. Calparsoro applied SEM-EDS for characterizing several building materials with black crust and dirt surfaces of a small construction called "malacate" in order to assess the main weathering phenomena suffered by the building [10]. Ostrooumov used XRD to characterize monument damage in historical monuments in Morelia (Mexico). The research team studied 43 samples of volcanic debris and volcanic rocks (pyroclasts) from two former monasteries in San Francisco and San Agustín in the city of Morelia [11]. Clark studied the red pigments of iron oxide red and ceramic shards from southern Italy using micro-Raman techniques, and the results obtained were important for further conservation [12].

Our study adopts an interdisciplinary approach comprising the analysis of historical archives and physicochemical properties. While this paper represents a preliminary investigation of the history and characteristics of clinker bricks, it provides the basis to discuss the heritage value of clinker bricks and to carry out further research about their manufacturing techniques and future conservation solutions.

2. Material and Methods

The clinker bricks are sampled from the facades of the Smart Memorial Gymnasium. The sampling has been authorized by the University administrator. Their characterization mainly targeted their physicochemical properties, ranging from chemical composition to water absorption coefficient. Since the exposed clinker bricks in the Smart Memorial Gymnasium can be classified into several different types based on their morphological features, the sampling has encompassed the major types in order to examine their similarities and differences (Figure 4). Information of the samples and their macroscopic characteristics are given in Table 1.

Table 1. Brick sample mark, location and macroscopic observation.

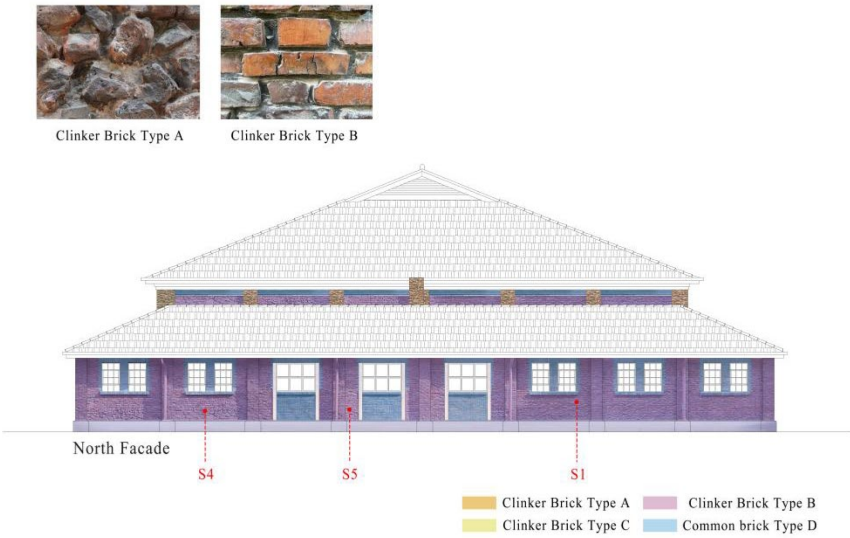
Sample	Location	Dimension [mm]	Color and Texture	Image
S1	North facade	50 × 55 × 34	Red with brownish tinge and white–grey marbled texture	
S2	East facade	23 × 26 × 6	Red with white–grey coarse grain, network crack on the surface	
S3	West facade	32 × 67 × 12	Dark red with vitrified texture	
S4	North facade	15 × 20 × 4	Peeled-off fragments, coarse with grains of varied colors in section, from white–grey to black, minor vitrified texture in the cavities	
S5	North facade	23 × 26 × 14	Coarse with grains of varied colors in sections, from white–grey to black (the same type with S4, coarser than S7)	
S6	East facade	34 × 37 × 11	Red with grey–black section	
S7	South facade	24 × 33 × 10	Grey–black section with yellowish tinge	

Heritage material analysis is inherently interdisciplinary, given that it combines historical, chemical, and physical analysis. The present study follows these three lines of examination in this same order.

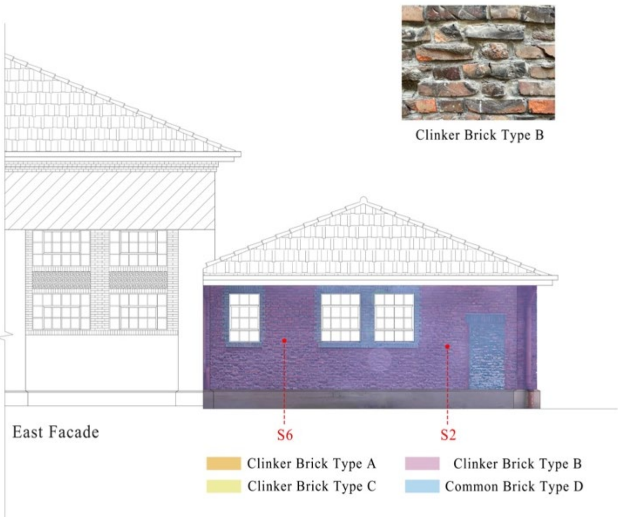
i. The first line of examination explores the contemporary knowledge of clinker bricks, based on historical sources from the 19th and 20th centuries, focusing on their perceived features and architectural applications (from a social-cultural perspective), as well as their raw materials mixtures and manufacturing processes (from a technological perspective). Due to the lack of direct historical sources regarding clinker bricks in China, it is essential to carry out a historical survey of clinker bricks in the British and American literature to explore the similarities and unique features of this foreign-inspired but locally manufactured heritage material in China. Historical methods are mainly used for this section. The main sources include: (a) United Board for Christian Higher Education in Asia Records about Dong Wu Da Xue, held at the Divinity Library, Yale University (United States); (b) historical records related to construction and restoration held in the Soochow University Archives and Suzhou Municipal Archives; (c) a comprehensive analytical record of the 14 oldest university buildings in the Tiancizhuang Campus (2019); (d) early printed architectural dictionaries, building books and construction magazines from the 19th and 20th centuries in Britain and United States, such as Nicholson's *An Architectural Dictionary* (1819), Searle's *Cement, concrete and bricks* (1926), the famous British journal of architecture *The Builder* (published between 1843–1966), and the American trade magazine on building and construction *The American Builder* (published between 1917–1969).

ii. The second line of examination pursues the characterization of clinker bricks used in the Smart Memorial Gymnasium, which provides an understanding of the chemical compositions of the tested clinker brick samples. The findings of this section are later discussed in relation to the literature on the historical production of clinker bricks and the possible raw materials mixtures recorded in historical sources. The mineralogical composition was determined using an XRD system (model D8 Advance, Bruker, Bremen, Germany). The following test conditions were used: CuKα rays (λ = 0.154 nm), operating voltage (40 kV), operating current (40 mA), and scanning range (30° to 90°). XRD analysis was performed by comparison with a standard PDF card, while micro-chemical analysis was carried out on a fully automatic confocal micro-Raman spectrometer model XploRA PLUS, manufactured by Horiba Jobin Yvon (Kyoto, Japan). The following test conditions were used: 532 nm laser with a power of 3.72 mW reaching the sample surface, Olympus 50x long working distance lens (Tokyo, Japan), and 1200 g/mm grating. Raman analysis for the characteristic peak of materials was performed by comparison with Raman spectra of pure standard compounds collected in the freely available Raman database [13] and the RRUFF database [14]. The elemental composition of the samples was analyzed using an SEM-EDS model SU8010 from Hitachi, Ibaraki, Japan.

iii. The third line of examination explores the physical performance and macro-scale characteristics of clinker bricks used in the Smart Memorial Gymnasium, with a focus on their water absorption. The findings of this macro-analytical characterization are correlated to the results from the microanalytical characterization (i.e., second line of examination, see above). Seven samples were examined by the total immersion test to determine their water absorption capacity $W_{AC} = (W_m - W_d) \times 100/Wd$ [15], imbibition capacity $IC = (W_m - W_d)/W_d$, and open porosity, where W_d is the dry weight and W_m is the saturated weight. The open porosity was calculated as the ratio of the volume of open pores (V_{op}) to the total sample volume (V_s). In our calculations from a practical point of view, it was calculated as the ratio of the weight of absorbed water to the density of water d, $(W_m - W_d)/d$. d was taken as 1 g/cm^3, that is, the density of water at 4 °C. The samples were oven-dried at 60 °C to constant weight for 15 h [16]. The weights of the dry samples were measured before their immersion in water for 24 h. After immersion, the samples were taken out of the container and dried with a paper towel, and their surface-dry weight was measured. The percentage change in weight was determined to quantify the water absorption coefficient.

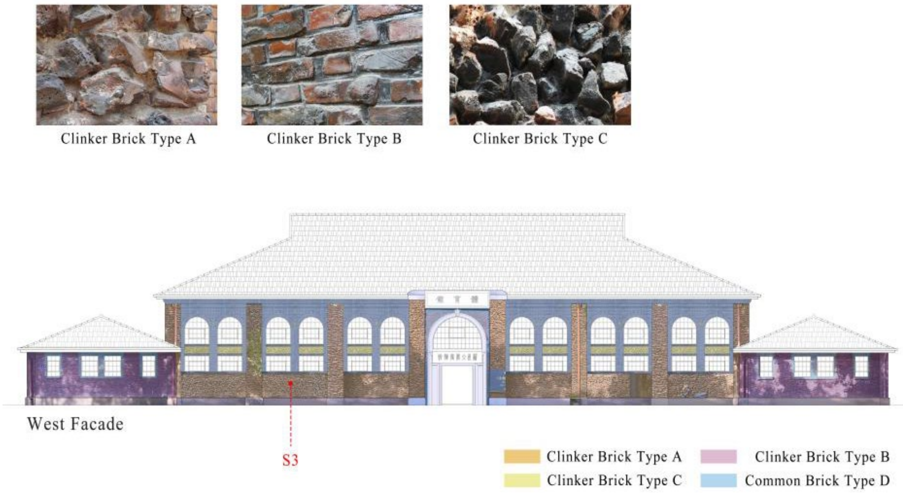


(**a**)



(**b**)

Figure 4. *Cont.*



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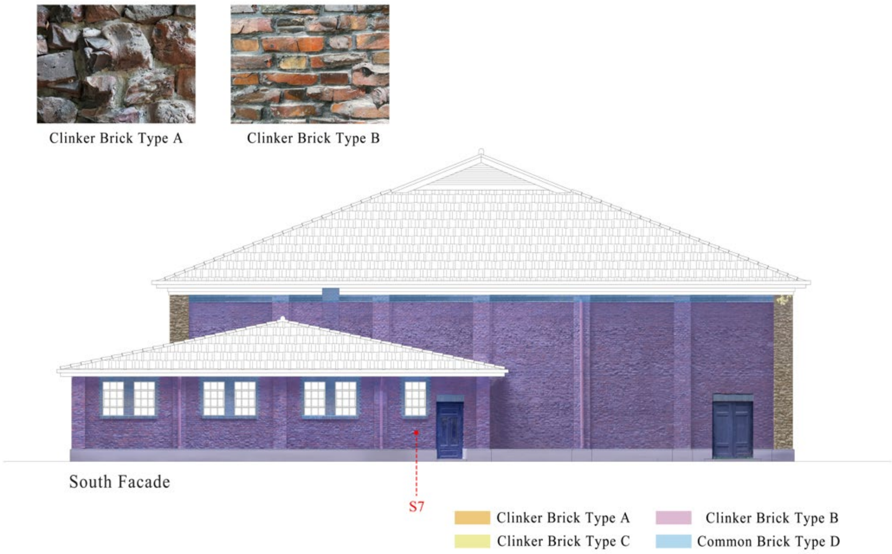


(**d**)

Figure 4. Morphological types of bricks and localization of the samples on the facades of the Smart Memorial Gymnasium. (**a**) North facade; (**b**) East facade; (**c**) West facade (main facade); (**d**) South facade.

3. Results and Discussion

3.1. Historical Analysis of the Clinker Bricks

The technical term "clinker" is a polyseme in historical literature. According to Searle (1926):

> "Crozzles, burrs and clinkers are bricks which have partly lost their shape through overheating. They have a vitrified texture and are heavy, dense, and "ring" when struck. The term clinker is also used for well-vitrified paving bricks of a good quality. This double use of the term is liable to prove confusing." [17] (p. 400)

Moreover, "clinker" could also refer to a nodular material produced in the kilning stage during the production of cement, but this definition is irrelevant to this paper.

(1) Clinkers as deformed bricks

The first definition of clinkers emphasizes the poor brickmaking process control, as the deformation of clinkers is unintentional, and thus undesired. The "clinkers" in the context of brickmaking in the 19th century in Britain were generally considered the opposite of "good bricks" and it was believed that their production should be prevented. In his *An*

Architectural Dictionary, Nicholson (1819) defined clinkers as a material that had been "too violently acted upon by the fire, have vitrified in the kiln, and sometimes several are found run together" [18] (p. 80). Lockwood (1845)'s paper "Bricks and Brickmaking" published in *The Builder* noted that sand and heat are the two main reasons leading to the formation of clinkers: "if there should be an excess of sharp, siliceous sand, it will run into a shapeless mass when in a state of vitrification: if it should be burned too much in this state, it will form what are called clinkers, which are produced by excess of heat and sand." [19] By observing the common brickmaking practice in the area of London and based on his own experience, Lockwood provided two solutions for reducing the occurrence of clinkers: (1) to "increase the chalk or similar 'holding' bodies" if there was too much sand in the clay; (2) and to "decrease to some extent the quantity of breeze (ash of coal, a very fine anthracite that aids firing) mixed with the clay", because, in Lockwood's opinion, the London brickmakers were "always anxious to burn their bricks as soon as possible", causing "an unnecessary amount of waste from clinkers and imperfectly burned bricks".

(2) Clinkers as good engineering and paving bricks

The second definition of clinkers emphasizes a certain degree of process control in order to produce good engineering and paving bricks. In his *An Architectural Dictionary*, Nicholson (1819) hinted at this intention and control as he wrote about "bricks impregnated with a considerable quantity of nitre or salt-petre, and placed next to the fire in the clamp, or kiln, that they may be more thoroughly burnt" [18] (p. 261). Similarly, Searle (1926) revealed such process control:

(1) in terms of ingredients

> "Engineering, clinker and paving bricks are made of somewhat fusible clays which are able to retain their shape at a high temperature, notwithstanding the larger amount of vitrification which takes place. They own their strength to the tenacity with which the infusible particles in the clay are bound together by the more fusible constituents." [17] (p. 335)

(2) in terms of temperature

> "Where the heating is pushed to the fullest extent possible without loss of shape, the material will be found to resemble an opaque glass or slag in character. It will be excessively hard, entirely impervious to water and highly resistant to corrosive acids. It's colour will be dark, approaching a brownish black, a slag grey, or what is known technically as a clinker, or Staffordshire blue, and its density will be appreciably increased." [17] (p. 396).

Clinkers were normally categorized based on their production origin (i.e., Dutch clinkers, Flemish clinkers, English Clinkers) [20,21]. The term "Dutch clinkers" refers to a popular type of clinker bricks for pavement imported from Holland. For instance, Dutch clinkers were used in the construction of the flooring of the Royal Stables at Windsor, UK, in 1839–1842 [22]. With respect to their uses, clinkers commonly appeared as a type of paving brick in the commercial advertisements in the contemporary British building magazine *The Builder* in the 19th century [23–25]. Based on the account of Nicholson (1856), "The hardest kind of all [the paving bricks] are termed clinkers, and are chiefly used for paving yards, stables, &c., and in constructing ovens, lining soap-boilers, cisterns, &c [26]." Related brick manufacturing technologies were introduced in China in the early 20th century, as the Kailuan Mining Administration developed a commercial product called "K.M.A. Clinkers", which was marketed as "a brick that will last for centuries" and "suitable for heavy foundation works, dock building, bridges, buildings & flooring". K.M.A. Clinkers were essentially an undeformed and good engineering material rather than a decorative material, and they were used for the construction of the Kailuan Mining Bureau Qinhuangdao Power Plant in 1928.

(3) Defect control for the optimization of clinker bricks

From the earliest unwanted “clinkers” to the later desired “clinker bricks”, the shift of terminology marked a transition in their manufacturing from a lack of technical control to an intentional defect control. The production of clinker bricks became intentional, aiming at deliberately producing more deformed clinker bricks for decorative brick walls. Based on the literature and historical sources available, we understand that, with the rise of the demand for decorative clinker bricks, some American manufacturers “experimented” to increase the output of clinker bricks [27]. However, little is known about the details of these manufacturing methods used to achieve these goals.

Our investigation of the contemporary knowledge of clinker bricks in the 19th and early 20th centuries is in itself insufficient to reconstruct the manufacturing methods of clinker bricks at that time. However, our investigation has revealed two possible directions to increase the output of clinker bricks: the control of the ingredients and the control of the temperature. Specifically, one possible method is to increase the comparative proportion of silica (SiO_2, in the form of sand), which increases the tendency of the brick in the kiln to fuse. On the contrary, increasing the comparative proportion of calcium carbonate ($CaCO_3$, in the form of chalk) would suppress the tendency of the brick in the kiln to fuse. In addition, nitre or salt-petre ($-NO_3$) can be added to brick clay, which can also be helpful to assist thorough burning. Apart from balancing the proportion of ingredients and thus changing the chemical composition of natural brick clay, one possible method is to add excess breeze to the brick clay to assist the burning process. Finally, an obvious possible method is to lay the bricks in the kiln close to the fire.

In the case of the Smart Memorial Gymnasium in Suzhou, it is important to note the contradiction between “overheating” for producing clinker bricks in the West and the required “slow heating” for the native “gold brick” manufacturing tradition in Suzhou. Historically, Suzhou brick craftsmen were renowned for their extensive experience in heat control and brick sorting for supplying the best-quality “gold bricks” for imperial building sites. Producing a perfect “gold brick” required a slow procedure consisting of 24 steps and more than 370 days, according to *Zaozhuan Tushuo* (1534), which highlighted the Suzhou brick craftsmen’s extraordinary attention to process control. By contrast, the production of clinker bricks with a fused appearance is commonly due to a lack of technical control and a rapid rise in temperature. Therefore, the contradiction between the use of clinker bricks and Suzhou brickmaking history suggests that the local brickyards in Suzhou deliberately produced clinker bricks for the Smart Memorial Gymnasium as a commissioned order, rather than because they lacked the knowledge for producing good bricks, although no direct evidence can be provided to date.

We will see later how the micro-analytical characterization of the clinker bricks from the Smart Memorial Gymnasium in Suzhou correlates to the traditional knowledge about clinker bricks.

3.2. Chemical Composition and Micro-Chemical Analysis

(1) Elemental analysis

The SEM-EDS spectra of samples S1–S7 from the Smart Memorial Gymnasium are quite similar; therefore, in Figure 5, we only present sample S1 as a representative. The SEM image (Figure 5a) supplies the surface micromorphology of sample S1. Figure 5b gives the elemental information from the local collecting point, which can be seen in the insert image. It is apparent that sample S1 has the highest elemental content of Si and O, and also contain trace amounts of C, N, Al, K, Na, Mg, Ca, Fe, and S. The elemental composition is also provided in Table 2. For samples S2–S7, the types of elements are the same, but the proportions are different.

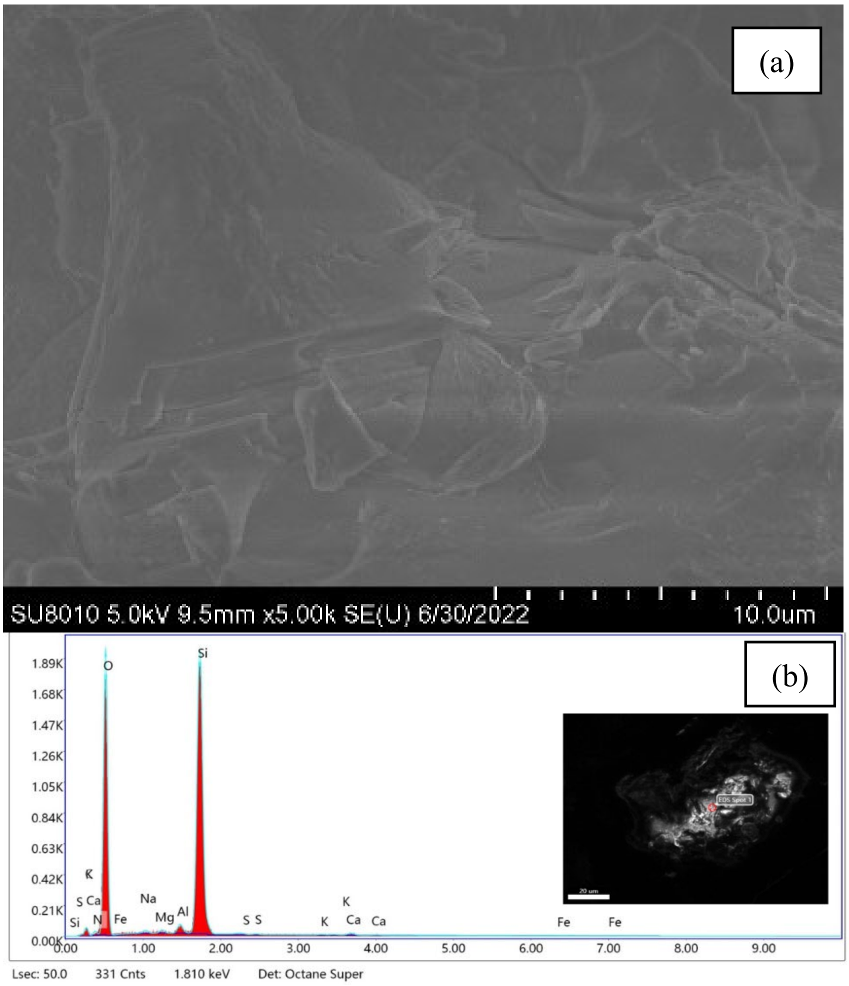


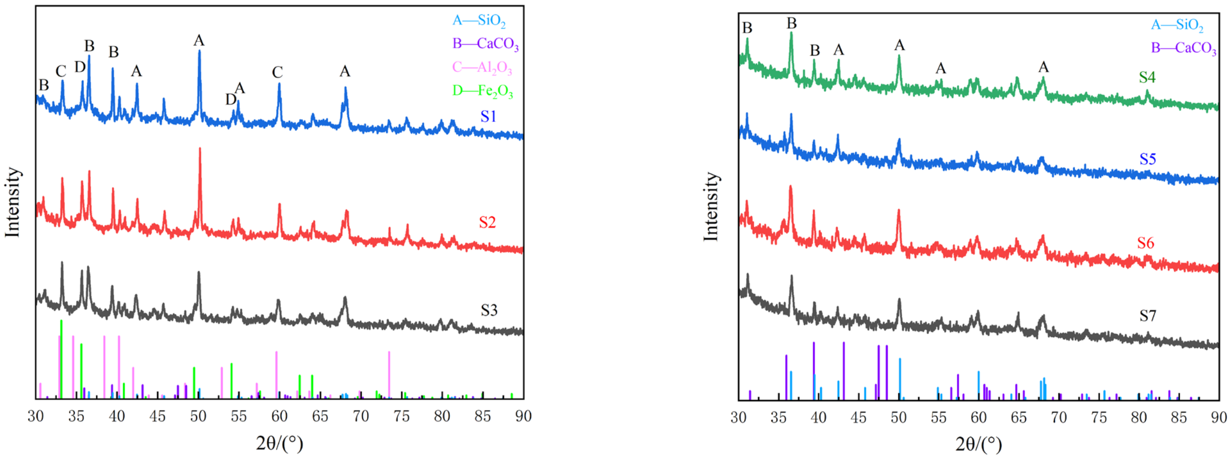
Figure 5. (**a**) SEM of the clinker brick (sample S1); (**b**) EDS of the clinker brick (sample S1); the inset image is the collecting point.

Table 2. Elemental composition from EDS spectra of the clinker brick (sample S1).

	Element	C	N	O	Na	Mg	Al	Si	S	K	Ca	Fe
S1	**Weight%**	6.03	2.26	56.44	0.70	0.51	1.07	31.97	0.07	0.15	0.54	0.25

(2) XRD analysis

Figure 6a shows the XRD of S1, S2, and S3. By comparing these analyses with standard PDF cards and combining them with elemental analysis results from EDS, we can observe the characteristic diffraction peaks of silicon dioxide (SiO_2) at 50°, calcium carbonate ($CaCO_3$) at 37°, aluminum oxide (Al_2O_3) at 33.6°, and iron oxide (Fe_2O_3) at 36°. Other diffraction peaks were also used for comprehensive discrimination of these samples. After careful analysis, SiO_2, $CaCO_3$, Al_2O_3, and Fe_2O_3 were inferred to be the main compounds originating from S1, S2, and S3 samples. In Figure 6b, from the XRD of S4, S5, S6, and S7, they can be mainly identified as SiO_2 and $CaCO_3$.

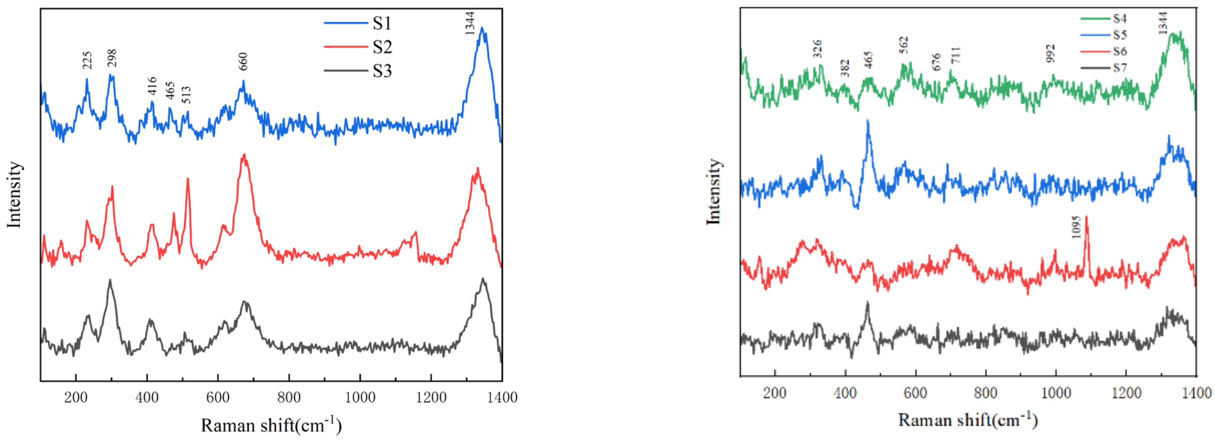


(**a**) (**b**)

Figure 6. Measured XRD patterns of the clinker bricks (traces labelled S1–S7): (**a**) S1–S3; (**b**) S4–S7. The standard XRD patterns for the identified compounds are also shown at the bottom of the plots.

(3) Raman spectroscopy analysis

In order to find the possible trace chemical composition, Raman spectroscopy technology with the reputation of fingerprint spectroscopy was introduced for further research. Raman tests were performed in the spectral range of 100–1400 cm^{-1}, with an integration time of 30 s and three integrations. Figure 7a shows the Raman spectra of S1, S2, and S3. Their spectra have some similarity. The peaks at 225 cm^{-1} and 291 cm^{-1} are assigned to hematite (Fe_2O_3) [28]. Similarly, the peaks at 298 cm^{-1} and 392 cm^{-1} are assigned to limonite (Fe_2O_4-H_2O) [9]. The peaks at 416 cm^{-1} and 660 cm^{-1} are from corundum (α-Al_2O_3) [14]. The peak at 465 cm^{-1} is ascribed to the bending vibration of the O-Si-O angle within the tetrahedra of quartz (SiO_2) [29]. Micro-plagioclase [30] ($KAlSi_3O_8$) is found at 513 cm^{-1}, and the whole Raman spectra attributed to micro-plagioclase ($KAlSi_3O_8$) are located at 184 cm^{-1}, 256 cm^{-1}, 454 cm^{-1}, 476 cm^{-1}, and 513 cm^{-1}.



(**a**) (**b**)

Figure 7. Raman spectra of clinker bricks. (**a**) S1–S3; (**b**) S4–S7.

Figure 7b shows the Raman spectra of S4, S5, S6, and S7. The peaks located at 326 cm^{-1}, 626 cm^{-1},and 853 cm^{-1} are consistent with the scattering peaks of tricalcium aluminate ($3CaO{\cdot}Al_2O_3$). The peaks at 382 cm^{-1}, 676 cm^{-1} and 725 cm^{-1} can be attributed to magnetite (Fe_3O_4). At 280 cm^{-1}, 711 cm^{-1}, and 1086 cm^{-1} are the characteristic scattering peaks of calcite [31]. Specifically, 711 cm^{-1} corresponds to the ion translation and vibration of CO_3^{2-}, indicating that calcium carbonate ($CaCO_3$) is the main chemical composition of calcite in the sample, while 1086 cm^{-1} and 280 cm^{-1} correspond to the symmetric stretching and outward vibrational mode of CO_3^{2-}, respectively. It should be noted that a peak at 1095 cm^{-1} of S6 is more pronounced for dolomite [32] ($CaMg(CO_3)_2$). The peak can be assigned to the symmetric stretching mode of CO_3^{2-}. To sum up, compared with XRD, Raman spectroscopy can obtain more chemical compositions of clinker bricks.

3.3. Physical Characteristics: Water Absorption Coefficient

With regard to the chemical analysis of different types of clinker bricks used in the Smart Memorial Gymnasium, it is possible to determine the mineralogical composition of the raw clay. Furthermore, we can also understand the relationship between the brick samples' morphological types, mineralogical composition, and water absorption coefficient.

Results of water absorption capacity, imbibition capacity, and open porosity of the samples are presented in Table 3 and Figure 8.

Table 3. Water absorption capacity (WAC, weight per weight [wt./wt.]), imbibition capacity (IC, [wt./wt.]), and open porosity (vol./vol.) of samples.

Sample	WAC [%, wt./wt.]	IC [wt./wt.]	Open Porosity (%, vol./vol.)
S1	13.66	0.137	0.62
S2	27.67	0.277	1.55
S3	6.69	0.067	0.72
S4	6.25	0.063	0.2
S5	18.79	0.188	0.59
S6	13.22	0.132	0.96
S7	14.24	0.142	0.47

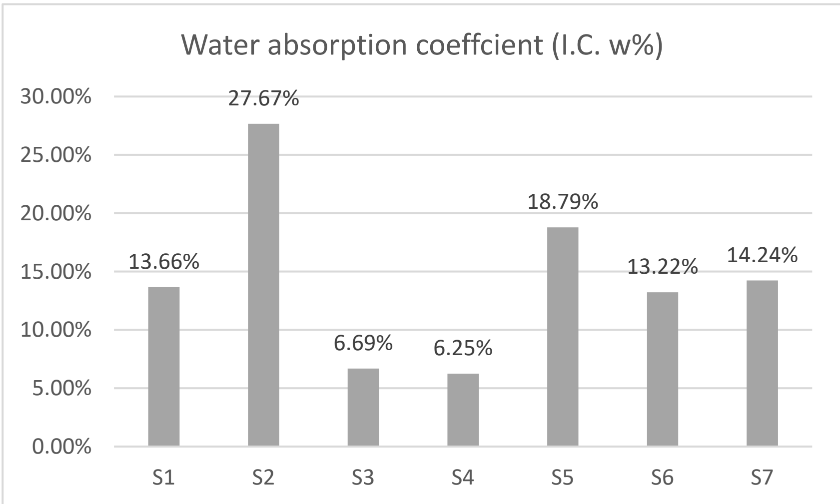


Figure 8. Water absorption coefficient of 7 samples.

The open porosity of S2 is approximately eight times that of S4, while S1, S5, and S7 have similar open porosity. It is essential to note that the open porosity in our discourse does not represent the total porosity (unless the material absorbs water in vacuo). The open porosity is regarded as a more practical parameter for construction material.

The water absorption coefficient of historical bricks showed in the range of 12–16% [33]. The brick samples S2 and S5 were found to have higher values (27.67% and 18.79%), whereas the brick samples S3 and S4 had lower values (6.69% and 6.25%). S1, S6, and S7 had very similar water absorption coefficients. Water absorption indirectly represented the capillary or water-accessible interconnected pores in the system [34]. Brick sample S2 showed the highest water absorption coefficient due to the network shrinkage on the surface, whereas brick sample S3 reported a lower water absorption coefficient than most historical bricks, due to the vitrified texture.

4. Conclusions

Although the complex history and features of clinker bricks prevent their exhaustive treatment within a single study, the present research provides fresh insights into the characteristics and values of historical clinker bricks used in the Smart Memorial Gymnasium of Soochow University in China. These findings lay a foundation for the heritage recognition of Chinese clinker bricks and the conservation of the Smart Memorial Gymnasium.

i. Prior literature tends to describe clinker bricks as a material with superior physical properties, being more resistant to water and less subject to powdering. However, our research points out that this statement is not fully reliable. Compared with common bricks, clinker bricks are far from being a homogeneous material but are rather a complex heterogenous material. In fact, different parts of the same clinker brick may exhibit different material characteristics from microscopic to macroscopic scales. This is the reason why it is essential to carry out sampling at multiple clinker brick locations of the same building. Our physicochemical characterization results prove that the properties of the clinker bricks from the Smart Memorial Gymnasium vary widely. So far, there is no legal recognition or technical regulation of this particular type of material (i.e., clinker bricks) in China. The most relevant legal reference is the Chinese conservation Trade Standard titled "Material for maintenance and conservation of historic architecture—Grey brick" (WW/T 0049-2014) issued by the State Administration of Cultural Heritage of P.R. China and implemented on 2014-06-01. It covers grey bricks, but makes no mention of clinker bricks. The lack of legal recognition or technical specifications for clinker bricks further demonstrates the importance of research into historical clinker bricks for the improvement of relevant technical regulations in the future, as well as the conversation regarding relevant historical buildings.
ii. Our investigation of the knowledge of brickmaking in the 19th and 20th centuries reveals a good understanding of the process control for producing good bricks in British and American historical literature. The chemical composition of natural clays could be altered by the appropriate addition of ingredients. Specifically, the historical literature mentions three additive ingredients (i.e., siliceous sand; the chalk or similar 'holding' bodies"; and nitre or salt-petre) to obtain the desired final results, i.e., to increase the output of good bricks and avoid clinkers. In addition to ingredient control, temperature control was also essential in brick-making practice as a means of reducing or increasing the production of clinkers.
iii. The analysis of mineralogical composition reveals that the raw clays of the clinker bricks used in the Smart Memorial Gymnasium came from at least two different sources. Arguably, they may have come from two different brickyards, or they may have been produced by mixing different additives at two different times in the same brickyard. Clinker brick samples S1–S3 came from raw clay 1, and they contain high quartz, and relatively low calcite. Clinker brick samples S4–S7 came from raw clay 2, and by contrast, they contain low quartz, and relatively high calcite.
iv. Our results of the physicochemical analysis are generally consistent with the knowledge of clinker bricks in 19th and early 20th century. The mineralogical composition indicated that the raw clay of brick samples was a layered silty clay. In the case of clinker bricks of raw clay 1, the high quartz content (which may be achieved by adding an excess of siliceous sand into the clay earth) played a decisive role in increasing the tendency of the bricks to fuse in the kiln. In the case of clinker bricks of raw clay 2, the high calcite content countered the tendency of the bricks to fuse in the kiln. The result was that both sample S3 (of raw clay 1, although S3 was fused with a higher degree of vitrification) and sample S4 (of raw clay 2, with a minor degree of vitrification) achieved the lowest water absorption coefficient (about 6%) compared to the rest

of the samples (about 13~28%). However, sample S2 (of raw clay 1) showed high fissuring on the surface, leading to the highest water absorption coefficient.

v. The brick samples were collected from different morphological types on four facades of the Smart Memorial Gymnasium. However, our study reveals that the mineralogical composition of the bricks does not correspond to their morphological classification. This is because, apart from ingredient control, temperature control also plays a crucial role in shaping the morphological features of the finished bricks. This explains why clinker bricks of raw clay 1 consist of both more regular-shaped bricks (samples S1 and S2 from the north and east facades), as well as fused bricks (sample S3 from the west facade). The differences in their appearances may have been the result of different firing temperatures.

vi. The various material characteristics will influence the selection of repair methods and conservation products in the future. (1) Heterogeneity: Our research has shown that, compared with common bricks, historical clinker bricks are far from a homogeneous material. Historical clinker bricks should be treated as a complex heterogeneous material during restoration and maintenance. (2) Porosity and salts: Given the higher porosity of historical clinker bricks compared to modern clinker bricks, soluble salts may be one of the most harmful causes of clinker brick degradation. Restoration professionals should pay extra attention to the presence of salts. (3) Brick sorting and selection: The west facade is the main facade of the Smart Memorial Gymnasium. Therefore, the west facade is architecturally more important and contains more decorative arrangements and elements. Our research has shown that the clinker bricks used on the west facade generally have better quality (e.g., low water absorption coefficient). Restoration professionals should take into account that, during construction of the Smart Memorial Gymnasium, the builders probably gave priority to the west facade when they were sorting and selecting clinker bricks for use. (4) Historical material replacement: for the purpose of replacing the severely damaged historical clinker bricks during restoration, further investigation into their historical chemical composition and characteristics is important to manufacture replacement clinker bricks.

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