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Study of Sticky Rice−Lime Mortar Technology for the Restoration of Historical Masonry Construction

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CONSPECTUS

Replacing or repairing masonry mortar is usually necessary in the restoration of historical constructions, but the selection of a proper mortar is often problematic. An inappropriate choice can lead to failure of the restoration work, and perhaps even further damage. Thus, a thorough understanding of the original mortar technology and the fabrication of appropriate replacement materials are important research goals.

Many kinds of materials have been used over the years in masonry mortars, and the technology has gradually evolved from the single-component mortar of ancient times to hybrid versions containing several ingredients. Beginning in 2450 BCE, lime was used as masonry mortar in Europe. In the Roman era, ground volcanic ash, brick powder, and ceramic chip were added to lime mortar, greatly improving performance. Because of its superior properties, the use of this hydraulic (that is, capable of setting underwater) mortar spread, and it was adopted throughout Europe and western Asia. Perhaps because of the absence of natural materials such as volcanic ash, hydraulic mortar technology was not developed in ancient China. However, a special inorganic−organic composite building material, sticky rice−lime mortar, was developed. This technology was extensively used in important buildings, such as tombs, in urban constructions, and even in water conservancy facilities. It may be the first widespread inorganic−organic composite mortar technology in China, or even in the world. In this Account, we discuss the origins, analysis, performance, and utility in historic preservation of sticky rice−lime mortar.

Mortar samples from ancient constructions were analyzed by both chemical methods (including the iodine starch test and the acid attack experiment) and instrumental methods (including thermogravimetric differential scanning calorimetry, X-ray diffraction, Fourier transform infrared, and scanning electron microscopy). These analytical results show that the ancient masonry mortar is a special organic−inorganic composite material. The inorganic component is calcium carbonate, and the organic component is amylopectin, which is presumably derived from the sticky rice soup added to the mortar.

A systematic study of sticky rice−lime mortar technology was conducted to help determine the proper courses of action in restoring ancient buildings. Lime mortars with varying sticky rice content were prepared and tested. The physical properties, mechanical strength, and compatibility of lime mortar were found to be significantly improved by the introduction of sticky rice, suggesting that sticky rice−lime mortar is a suitable material for repairing mortar in ancient masonry. Moreover, the amylopectin in the lime mortar was found to act as an inhibitor; the growth of the calcium carbonate crystals is controlled by its presence, and a compact structure results, which may explain the enhanced performance of this organic−inorganic composite compared to single-component lime mortar.

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1. Introduction

Many kinds of mortars have been ever since ancient times. Among them, mud mortar seems to be the first[1] employed in ancient buildings, which is still in use now all over the world. Gypsum and asphalt[2] were used for joints of bricks and stones. However, gypsum between the stone blocks was generally not regarded as mortar, but mainly as a lubricant.[3] The calcination of limestone was discovered in 2450 BC[1] in Europe. After that, lime was used as an important constituent of mortars. Early in ancient Greece, lime mortar was used in construction.[4] In Roman times, mortar technology was greatly improved and hybrid mortars like lime–sand and lime–gypsum[5] mortar appeared. Later, hydraulic materials such as ground volcanic ash, ceramic chip, and ground brick[6] were introduced. This kind of hydraulic mortar was called "Roman mortar"[7] and was extensively used in Europe and western Asia until the appearance of modern cement in the 19th Century.

In China, there is also a long history of the use of lime; production of lime began ∼5000 years ago.[8] After the Qin and Han dynasties, lime was used more widely. The famous "Straight Highway of Empire Qin" was rammed with lime and local loess.[9] At least in the Han dynasty, an inorganic hybrid mortar material named "Sanhetu" (composed of lime, clay, and sand) was invented, which is close to Roman mortar in terms of performance.[10] Tongwan city constructed with Sanhetu is so strong that it is "as hard as stone" and can be used to "sharpen knife and axe".[11] Even today, it is still in use in the construction of river banks.

Perhaps because of the absence of natural hydraulic materials like volcanic ash, hydraulic mortar technology was not developed in ancient China. However, distinctive inorganic–organic composite mortars were developed. Via addition of natural organic compounds like sticky rice soup, the juice of vegetable leaves, egg white, tung oil, fish oil, or animal blood,[12] the performance of lime mortars can be greatly improved, and these mortars are believed to play an important role inr the longevity of ancient Chinese buildings.[13] Among these mortars, sticky rice–lime mortar was the most widely used in the important buildings like city walls, palaces, tombs, and even water conservancy facilities. It may be the first extensively used organic–inorganic composite building material in China and even in the world.

However, the traditional sticky rice–lime mortar technology has not been fully studied from a scientific point of view, and few related works have been reported. In this Account, we present our recent study of the origins, analysis, performance, and utility of this special organic–inorganic composite mortar in the conservation of ancient masonry construction.

2. Sticky Rice–Lime Mortar Technology and Its Application in Ancient Construction

The earliest record of sticky rice–lime mortar was seen in the ancient building work "Tian Gong Kai Wu",[12] which was written during the Ming Dynasty (1368–1644 AD). In fact, according to the archeological evidence,[14] sticky rice–lime mortar was already a mature technology no later than the South-North Dynasty (386–589 AD). Because of its good performance,[15] sticky rice–lime mortar was extensively used in many important buildings, such as tombs, city walls, and water resource facilities. Early in the South-North Dynasty, it was used in tomb building, for example, the brick tomb in Deng County, Henan Province.[14] From the Song Dynasty to the Qing Dynasty, sticky rice–lime mortar was more commonly used in the construction of tombs which were specially named the "lime compartments".[16] In 1978, the tomb of Xu Pu and his wife was found. This lime compartment tomb built during the Ming Dynasty is so firm that a bulldozer could do nothing about it.[17] Some ancient stupas, temples, and bridges in Quan County built with sticky rice–lime mortar even survived the 7.5 grade earthquake of 1604 AD.[18] Many ancient city walls, including the Nanjing city wall of the Ming Dynasty, the Jingzhou city wall of the Ming Dynasty, and the Haizhou city wall of the Song Dynasty,[19] were all constructed with sticky rice–lime mortar. Moreover, sticky rice–lime mortar was used in river banks, such as the bank of Shaogong during the Ming Dynasty, the bank of Qiantang River during the Qing Dynasty, and the bank of the Lugou River.[20] Sticky rice–lime mortar was also used to build bridges, including the Tianjin bridge of the Ming Dynasty in Jiangsu Province,[21] the Mingyuan bridge of the Song Dynasty in Guangdong Province,[22] and the Xiandu bridge in Hubei Province.[23] Until modern times, sticky rice–lime mortar was still in use, for example, Kaiping turrent[24] in Guangdong Province and enclosed storied buildings in Fujan Province.[25] Most of the ancient buildings mentioned above are all in good repair today.

3. Analytical Study of Sticky Rice–Lime Mortar Used in Ancient Buildings

Ancient masonry mortar samples were obtained from the Nanjing city wall of the Ming Dynasty. According to the latest experimental measurement, the ancient Nanjing city wall is ∼33.7 km long, 10.0–18.0 m wide, and 12.0 m high and is believed to be the largest brick masonry ancient architecture

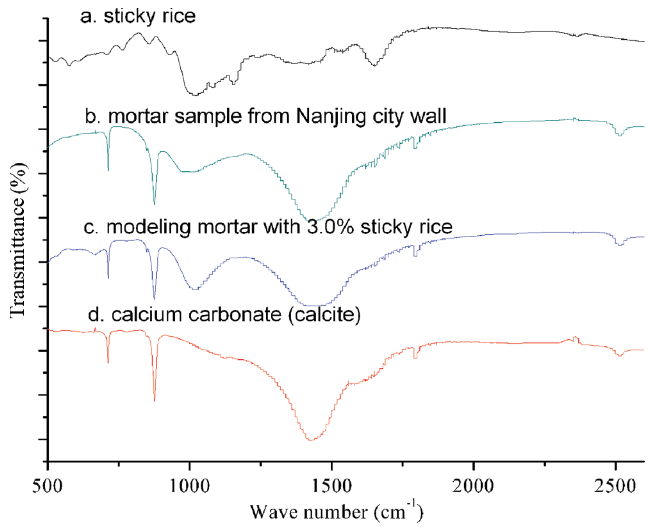

FIGURE 1. FTIR curves for sticky rice, mortar samples, and calcium carbonate (calcite).

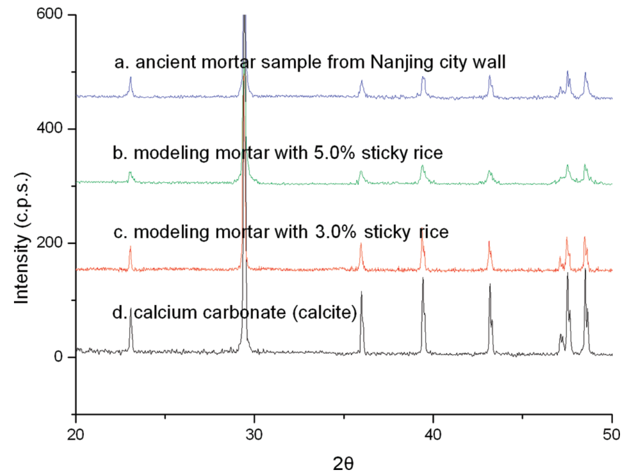

FIGURE 2. XRD patterns of mortar samples and calcium carbonate (calcite).

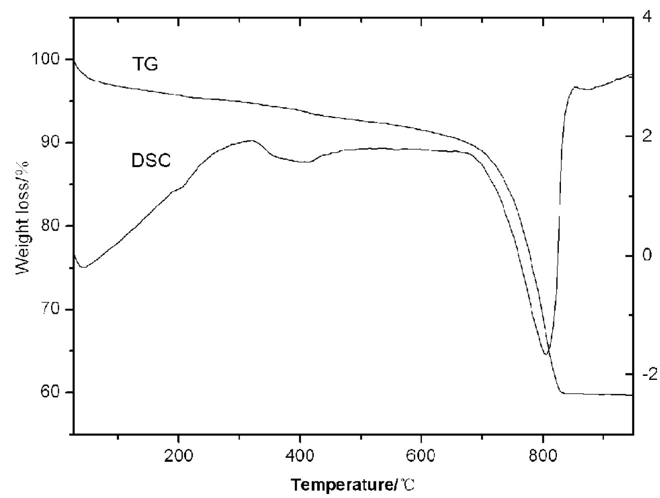

FIGURE 3. TG-DSC curves of mortar samples obtained from the Nanjing city wall.

in the world.[26] The ancient mortar samples were analyzed by both chemical analysis methods (including the iodine–starch test and the acid attack experiment) and instrumental analysis methods [such as thermogravimetric differential scanning calorimetry (TG-DSC), X-ray diffraction (XRD), Fourier transform infrared (FTIR), and scanning electron microscopy (SEM)].

The FTIR results for sticky rice (a), the mortar sample of the Nanjing city wall (b), and calcite (d) are given in Figure 1. The absorbance bands at 712, 876, 1429, 1794, and 2513 cm^{-1} are assigned to the calcite. These absorbance bands also appear in Figure 1b, suggesting that there is calcite in the ancient mortar. For sticky rice, the adsorption bands at 847 and 761 cm^{-1} can be attributed to the absorbance of the $-CH_2$ group, the adsorption bands at 1000–1154 cm^{-1} can be attributed to the absorbance of the C–O group from the glucose anhydride ring, and the adsorption bands at 1654 cm^{-1} can be attributed to the absorbance of the –OH group.[27] In Figure 1b, there are no $-CH_2$ adsorption bands of sticky rice at 761 and 847 cm^{-1}, due to the influence of adjacent strong calcite adsorption bands at 712 and 876 cm^{-1}. However, the C–O adsorption bands of the glucose anhydride ring at 1000–1154 cm^{-1} are still observed, suggesting the presence of sticky rice in the ancient mortar.

To further confirm the presence of sticky rice, a starch–iodine test was conducted. The red brown[28] was very evident after the addition of the iodine–KI reagent in the mortar suspension. It indicates that sticky rice is still present in the historical mortars.

The XRD results of the ancient mortar sample and calcite are presented in traces a and d of Figure 2, respectively. Obviously, the main component of the ancient sample is calcite, which is consistent with the FTIR results. However, the intensity of the diffraction peaks of the historical sample is weaker than that of pure calcite, suggesting that there may be amorphous calcium carbonate in the historic mortar sample besides calcite.

The TG-DSC results for the mortar sample are given in Figure 3. In the DSC curve, two endothermic peaks at 30 and 800 °C and an exothermic peak at ~320 °C can be observed. The endothermic peaks at 30 and 800 °C can be attributed to the evaporation of free water and the decomposition of $CaCO_3$,[29] respectively. The exothermic peak around 320 °C can be attributed to the decomposition of sticky rice. In an oxygen atmosphere, the main component of sticky rice, amylopectin, begins to decompose at ~320 °C and more than 94% of has decomposed by the time the temperature reaches 400 °C.[30] The content of $CaCO_3$ and sticky rice can be estimated from the percentage of weight loss of TG curves. In the temperature range from 320 to 400 °C, the weight loss is due

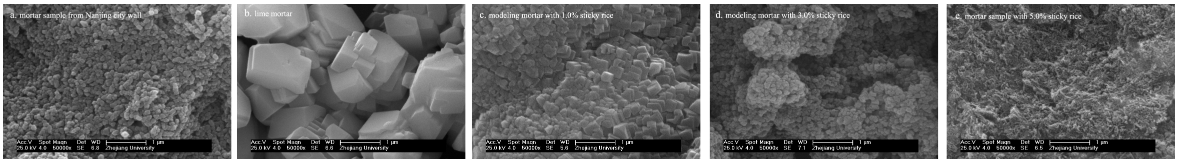

FIGURE 4. SEM images of mortar samples.

to the decomposition of sticky rice, and the weight loss between 600 and 800 °C is due to the decomposition of $CaCO_3$. According to TG data, the calculated contents of $CaCO_3$ and sticky rice in the mortar samples are ~75.0−81.0 and ~1.0−1.2%, respectively.

According to the analytical results described above, the mortar used in the Nanjing ancient city wall is an inorganic−organic composite construction material mainly composed of calcium carbonate and sticky rice. Besides the Nanjing ancient city wall, this kind of mortar has also been found in the pagodas of the Song and Ming dynasties,[31] the memorial arch of the Qing Dynasty,[32] and the city walls of the Ming Dynasty in Xi'an[33] in recent years.

4. Scientification of Sticky Rice−Lime Mortar Technology

Although commonly used in ancient buildings, there are few scientific studies of sticky rice−lime mortar technology and its application in the literature. For this section, the modeling sticky rice−lime mortar was fabricated and analyzed, and the role sticky rice played in the sticky rice−lime mortar was explored. Moreover, for their application in restoration, mortars with different ratios of lime to sticky rice soup were fabricated and their performance was evaluated.

4.1. Analysis of Modeling Sticky Rice−Lime Mortar. The mortar was made by evenly mixing slaked lime with sticky rice soup. We made a sticky rice solution by cooking a mixture of sticky rice powder and distilled water at 100 °C and 1.0 bar for 4 h. Before any analysis, mortar samples were naturally carbonized at 20 °C under 60 ± 5% relative humidity for 6 months. The results for hardened sticky rice−lime mortar are listed below.

The FTIR curve of modeling mortar (Figure 1c) is similar with that of the ancient mortar samples (Figure 1b). Both of them possess the characteristic peaks (712, 876, 1429, 1794, and 2513 cm^{-1}) of calcite and sticky rice (1000−1154 cm^{-1}), suggesting they have the same compositions. Besides, in modeling mortar and ancient mortar samples, the C−O adsorption bands of the glucose anhydride ring at 1000−1154 cm^{-1} are narrowed down, and the −OH adsorption bands at 1654 cm^{-1} disappear. These are the result of the interaction between sticky rice polysaccharide and calcium carbonate.[34] The XRD results of modeling mortar are given in traces b and c of Figure 2. Obviously, all the calcium hydroxides in the modeling mortar have been converted into calcite, which is consistent with the FTIR results presented in Figure 2c. In general, a polysaccharide additive in calcium hydroxide facilitates the formation of calcite, the thermodynamically preferred polymorph, and in the presence of amylose, almost 100% of the calcite can be obtained.[35] Furthermore, the modeling mortar samples with sticky rice exhibit lower-intensity calcite peaks, and the diffraction peaks are slightly broad (Figure 2b,c). This may be due to the presence of amorphous calcium carbonate or the nano-size calcite crystals.

The effects of sticky rice on the morphology of the mortar samples were also studied (Figure 4). For the pure lime mortar, macro-calcite crystals can be observed, but the structure is loose (Figure 4b). When 1.0% sticky rice is added to the mortar, the shape becomes irregular, the size of the crystal is reduced, and the crystal particles begin to stick together: a compact structure is produced (Figure 4c). The morphology change may be due to the specific interactions between the polysaccharide and calcium carbonate crystal.[35] The decrease in the particle size, however, may be the result of the higher viscosity of the additive.[36] For the modeling sample prepared with 3.0% sticky rice, the size of the calcite is further reduced and the morphology (Figure 4d) of it is very like that of the historical samples (Figure 4a), both exhibiting a compact microstructure, which should be the cause of the good performance of this kind of organic−inorganic hybrid mortar. When a 5.0% sticky rice solution is introduced, further changes in morphology occur and almost no crystal particles can be detected (Figure 4e). These results suggest that the sticky rice component in the lime mortar can act as an inhibitor and control the growth of the calcium carbonate crystal.

4.2. Performance of Sticky Rice−Lime Mortar. The fabricated sticky rice−lime mortar was tested according to the Standard Test Method of Performance on Building Mortar (JGJ/T70-2009).[37] For lime mortar, only limited water can be added to provide a suitable workability because an excess of water will strongly affect the mechanical properties of mortars.[38] Therefore, in this section, the ratio of water to lime is fixed at 0.8, which is close to that of the standard slaked lime.

TABLE 1. Properties of Fresh Mortars[a]

sticky rice soup content (%)	0.0	1.0	2.0	3.0
consistency (mm) (target range of 30–50)	55.0	43.2	37.1	30.0
water retentivity of fresh mortar (%)	85.5	91.6	93.4	93.7

[a] Ratio of water to lime of 0.8.

4.2.1. Consistency of Fresh Mortar. This test was performed according to JGJ/T70-2009, Part 4.[37] The results are presented in Table 1. According to the Specification for Mix Proportion Design of Masonry Mortar (JGJ 98-2000),[39] 30–50 mm of consistency is considered adequate for masonry mortars. Pure lime mortar has a consistency of ~55.0 mm, which means a high liquidity. High liquidity is favorable for rendering mortar, but for masonry mortar, it is unacceptable. Overly sloppy mortar is usually sneezed by massive building materials like brick and stone, leading to weakness of masonry buildings. Sticky rice soup, obviously, can work as a viscosity modifier and improve the consistency of lime mortar. When a 3.0% sticky rice soup solution is added, an adequate consistency (30 mm) can be obtained. In fact, polysaccharide viscosity modifiers have been extensively studied and used in cement and concrete.[40]

4.2.2. Water Retentivity of Fresh Mortar. The water retentivity of fresh mortar was measured according to JGJ/T70-2009, Part 7.[37] The results listed in Table 1 indicate that the water retentivity of lime mortar can also be improved by the addition of sticky rice soup. It seems that the more sticky rice is in the mortar, the better the water retentivity will be. This can be attributed to the water holding character of sticky rice amylopectin.[41] For lime mortar, high water retentivity is essential, because it can prevent quick suction of water by the background or its evaporation, which favors the carbonation reaction of lime and subsequent increase in mechanical strength.[42]

4.2.3. Shrinkage. Shrinkage was measured in the longitudinal dimension after the specimens were dried, according to JGJ/T70-2009, Part 12.[37] The test results of both lime mortar and sticky rice–lime mortar are presented in Figure 5. Obviously, lime mortar has a high shrinkage, which is the result of the rapid loss of water.[43] High shrinkage often leads to the cracking of mortar and weakening of the bond to the substrate. Thus, lime alone is usually not used as masonry or rendering mortars. In the presence of sticky rice soup, the shrinkability is restrained, and it seems that the more sticky rice is in the lime mortar, the lower the shrinkage will be. This also is due to the water holding character of sticky rice amylopectin. In fact, in the presence of aggregates like sand and gravel, the shrinkage of sticky rice–lime mortar can be decreased further.

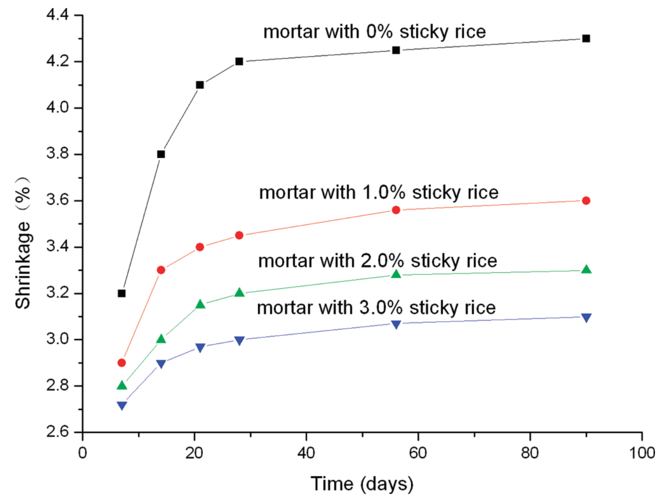

FIGURE 5. Shrinkage of modeling mortars.

TABLE 2. Bulk Densities of Fresh and Hardened Mortars

	0.0% sticky rice soup	1.0% sticky rice soup	2.0% sticky rice soup	3.0% sticky rice soup
bulk density of fresh mortar (kg/m^3)	1543.2	1477.7	1460.4	1452.2
dry bulk density of hardened mortar (kg/m^3)	1515.2	1432.6	1427.8	1402.7

4.2.4. Bulk Density of Fresh and Hardened Mortar. The test was performed according to JGJ/T70-2009, Part 5.[37] The results are listed in Table 2. We conclude that the bulk density of fresh lime mortar decreases with the content of sticky rice soup, suggesting that the mortar swells slightly in the presence of sticky rice soup. A similar phenomenon was observed by Chandra.[44] However, in his study, the reduction of bulk density is attributed to the air entrainment of proteins. In fact, the main component of sticky rice is amylopectin, a kind of polysaccharide, and the mechanism of the reduction of density may be different and need to be further studied. The dry bulk density of sticky rice–lime mortar is also slightly lower than that of pure lime mortars. This is consistent with the experimental results of the bulk density of fresh mortars and the shrinkage of hardened mortars.

4.2.5. Mechanical Strength of Hardened Mortar. The tests were performed according to JGJ/T70-2009, Parts 8–10.[37] The results presented in Table 3 suggest that the mechanical strength of lime mortar can be improved by the addition of sticky rice soup. For the lime mortar, the flexural, compressive, and adhesive strength are ~0.24, ~060, and ~0.25 MPa, respectively. However, when a 3.0% sticky rice solution is present, the strengths are improved gradually and reach maxima of 0.38, 0.94, and 0.50 MPa, respectively.

TABLE 3. Mechanical Strengths of Hardened Mortars

	0.0% sticky rice soup	1.0% sticky rice soup	2.0% sticky rice soup	3.0% sticky rice soup	4.0% sticky rice soup
flexural strength (MPa)	0.24	0.35	0.36	0.38	0.36
compressive strength (MPa)	0.60	0.82	0.907	0.94	0.93
adhesive strength (MPa)	0.25	0.42	0.48	0.50	0.49
modulus of elasticity (MPa)	1700	2250	2300	2400	2300

TABLE 4. Water Vapor Permeability and Water Absorption of Hardened Mortars

	0.0% sticky rice soup	1.0% sticky rice soup	2.0% sticky rice soup	3.0% sticky rice soup
water vapor permeability ($\times 10^{-11}$ kg m^{-2} s^{-1} Pa^{-1})	4.5	3.0	2.8	2.7
water absorption (%)	20.2	17.1	16.2	16.0

Nonetheless, there is not always a positive relation between the strength and the sticky rice content. The sticky rice component in moderation is helpful in the development of the strength of lime mortar, because its water retentivity favors the carbonation reaction of lime and the subsequent increase in mechanical strength.[45] However, organic matter in excess will work as a retarder and restrain the carbonization reaction[46] of lime mortar. Therefore, when there is a >3.0% sticky rice solution in the lime mortar, the development of the strength of lime mortar will be restrained.

The elasticity modulus of mortars was tested according to the Standard for Test Method of Performance on Building Mortar (JGJ/70-90), Part 8.[47] In the presence of sticky rice soup, the elasticity modulus of lime mortar is also improved (Table 3). When a 3.0% sticky rice soup solution is added, the elasticity modulus of lime mortar reaches its peak value of 2400 MPa. However, it is still far below the highest value of the elasticity modulus (1–18 GPa) of ancient brick,[48] which suggests that the sticky rice–lime mortar is characterized by an elastic behavior compatible with traditional masonry buildings.

4.2.6. Water Vapor Permeability of Hardened Mortar. The water vapor permeability of the hardened mortars was determined by the methodology described in EN 1015-19.[49] Results listed in Table 4 indicate that the water vapor permeability of lime mortar can be reduced by the addition of sticky rice. This is due to the compact structure of sticky rice–lime mortar. A reduced permeability is often a negative factor[50] for mortar, since it affects the elimination of water vapor that exists within buildings. However, even when a 3.0% sticky rice soup solution is introduced, the mortar can still have a high water vapor permeability of 2.7×10^{-11} kg m^{-2} s^{-1} Pa^{-1}. On the other hand, this may indicate other positive characteristics such as lower water absorption due to capillary action or even a lower permeability.

TABLE 5. Compatibilities of Mortar with a Clay Brick Substrate

	lime mortar	sticky rice–lime mortar
water permeability (mL)	750^a and 810^b	700^a and 690^b
adhesive strength (MPa)	0.25^a and 0.23^b	0.49^a and 0.49^b

^{a} Before climatic cycles. ^{b} After climatic cycles.

4.2.7. Water Absorption of Hardened Mortar. Water absorption of hardened mortar was measured according to JGJ/T70-2009, Part 14.[37] The results are listed in Table 4. It implies that the water adsorption of lime mortar can clearly be decreased via the addition of sticky rice soup. This is partly due to the compact structure of mortar, which is formed in the presence of sticky rice soup. In addition, the interaction between the sticky rice polysaccharide and the calcium carbonate may be another important factor. During the solidification of sticky rice–lime mortar, the hydrophilic hydroxyl group of amylopectin is covalently bonded by calcium cation[51] and the alkyl group may provide additional hydrophobicity. Low water absorption can protect the buildings against the erosion of water and soluble salt.[52]

4.2.8. Compatibility with Substrate. On the basis of EN 1015-21,[53] the compatibility of mortars was evaluated. The substrates were clay bricks, the most frequently used building materials in ancient Chinese construction. Before the test, the specimens were cured at 20 °C under 60 ± 5% relative humidity for 2 months. The effects of climatic cycles on the mortars were evaluated via water permeability and adhesive strength.

The test results are listed in Table 5. The permeability of sticky rice–lime mortar to liquid water is lower than that of lime mortar. For masonry mortar, a reduced permeability to liquid water is a positive factor, since it limits the penetration of water into the mortar. Besides, compared with lime mortar, sticky rice–lime mortar is less susceptible to climatic cycles. After artificial climatic cycles, the lime mortar deteriorates slightly in permeability (from 750 to 810 mL) and adhesive strength (from 0.25 to 0.23 MPa). The sticky rice–lime mortar, however, seems not to be affected. These results show that sticky rice–lime mortar is more compatible with brick substrates.

As a result, the performance of lime mortar can be significantly improved in the presence of an appropriate amount of sticky rice soup. Compared with lime mortar, sticky rice–lime mortar has more stable physical properties, has greater mechanical strength, and is more compatible with substrates, which make it a suitable restoration mortar for ancient masonry buildings.

5. Application of Sticky Rice–Lime Mortar in Historic Preservation

Sticky rice–lime mortar has been used in the restoration of some ancient masonry constructions. The Shouchang bridge is a single-arch stone bridge, built during the Song Dynasty, and is currently one of the national cultural heritage protection units.

The restoration work on the Shouchang bridge began in 2006. Because of bridge foundation settlement and plant growth, cracks between building blocks appeared and continued to widen in recent years. Necessary conservation, including the consolidation of the bridge foundation and bridge wall, removal of plants, and antiweathering treatment, was conducted. Sticky rice–lime mortar (made of slaked lime, sticky rice soup, and stone powder) was used as joint mortar. On the whole, sticky rice–lime mortar is the right choice. There are not any more cracks or desquamation after almost 5 years of exposure in the open air, indicating the good compatibility of sticky rice–lime mortar. Besides, there are no more plants in the mortar, and this may be attributed to the high alkalinity of slaked lime.

6. Conclusions

Sticky rice–lime mortar technology appeared at least 1500 years ago and was extensively adopted in ancient China. Analytical study shows that the ancient masonry mortar is a kind of special organic–inorganic composite material. The inorganic component is calcium carbonate, and the organic component is amylopectin, which should come from the sticky rice soup added to the mortar. Moreover, we found that amylopectin in the mortar acted as an inhibitor: the growth of the calcium carbonate crystal was controlled, and a compact microstructure was produced, which should be the cause of the good performance of this kind of organic–inorganic mortar. The test results of the modeling mortars show that sticky rice–lime mortar has more stable physical properties, has greater mechanical strength, and is more compatible, which make it a suitable restoration mortar for ancient masonry buildings.

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BIOGRAPHICAL INFORMATION

Fuwei Yang is a Ph.D. candidate in physical chemistry. His work is mainly focused on Chinese traditional building materials and the restoration and preservation of soil and stone heritage.

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Qinglin Ma is a professor of cultural relic preservation and vice president of the Chinese Academy of Cultural Heritage. His research interests include the reinforcing materials of wall painting, the preservation of metal antiquity, and paint in ancient wall painting and pottery.

APPENDIX A: EXPERIMENTAL DETAILS

7.1. Materials. KI, I_2, alcohol, deionized water, NaOH, acetic acid, KBr, $CaCO_3$, $Ca(OH)_2$, and NH_4HCO_3 (A.R. grade, ≥99.8% assay) were used in this study. Sticky rice, which is a type of rice grown in Southeast and East Asia mainly composed of amylopectin, is commercially available.

7.2. Sampling. The samples of historical mortars were obtained from the Nanjing ancient city wall from the Ming Dynasty just before its repair. The sampling positions are ~5–10 cm under the surface of the original mortar to ensure the samples are undisturbed.

7.3. Instrumentation and Operating Conditions. A NICOLET 560 Fourier transform infrared spectrometer was employed to identify the main molecular groups present in mortars, and the mortar samples were analyzed in KBr pellets. The spectra were traced in the range of 2500–500 cm^{-1}, and the band intensities were expressed in transmittance (percent). For the preparation of samples, 1–2 mg of the fraction of mortar was mixed homogeneously with 100 mg of anhydrous KBr in an agate mortar. A pressure of 10 ton was applied to this mixture to yield a transparent pellet. Identification is based on comparison of the bands of the recorded FTIR spectra with those of reference materials or from the literature.

For identification of the crystallography of the mortars, XRD analyses were performed with an AXS D8 ADVANCE X-ray diffractometer using Cu Kα radiation (λ = 1.54 Å), a voltage of 40 kV, and a current of 40 mA.

The thermal analyses were performed on simultaneous DSC-TG equipment (TA Instruments, model NETZSCH STA 409 PC/PG). The experimental conditions were as follows: (a) continuous heating from room temperature to 1000 °C at a heating rate of 20 °C/min, (b) air–gas dynamic atmosphere (45 cm^3/min), (c) alumina, top-opened crucible, and (d) a sample mass of ~15 mg.

The surface morphology of the mortar samples was inspected with an optical microscope and scanning electron microscopy (SEM, FEI SIRION-100).

In addition, the consistency of fresh mortar was determined with an SC145 mortar consistency tester. The shrinkage of mortar was measured in the longitudinal dimension with an SP-175 mortar contraction detector. The strength test of modeling mortar was conducted with a Yinchi (Shanghai, China) YC-125B tension meter.

7.4. Methods. Approximately 100 g of the historical mortar sample was ground in an agate mortar, and the fine powder obtained was analyzed by FTIR, XRD, and thermal analysis (TG-DSC). Next, the starch–iodine test was employed to confirm the amylopectin component of the mortar.

For the starch–iodine test, 5.0 g of the ground mortar sample was added to 100 mL of deionized water and the mixture heated at 80–90 °C for 10 min with stirring. The formed suspension was then cooled to 25 °C and its pH adjusted to 6.0–7.0 with acetic acid. We created the iodine–KI reagent by dissolving 0.2 g of iodine in 100 mL of deionized water in the presence of 2.0 g of KI. The iodine–KI reagent was dropped into the suspension, and a blue or red brown color (blue for amylose and red brown for amylopectin) was observed if starch existed.

We made a sticky rice solution by cooking a mixture of sticky rice powder and distilled water at 100 °C and 1.0 bar for 4 h.

For the hydration of quick lime, calcium oxide powder was added to water (quick lime:water mass ratio of 1:3) with agitation and the slaking temperature was held at 80 $\pm$ 10 °C. The lime putty obtained was stored for 6 months in an airtight container before being used.

To take a deeper look at the historical mortars, several modeling samples with 0, 1.0, 2.0, 3.0, and 5.0% sticky rice were fabricated and dried at room temperature under 60 $\pm$ 5% relative humidity. Six months later, the modeling samples were analyzed by FTIR, XRD, and SEM under the same conditions used for the historical samples.

For the specimens for the strength test, slaked lime, sticky rice soup, and deionized water were evenly blended and added to the cube-shaped mold (70.7 mm $\times$ 70.7 mm $\times$ 70.7 mm). The specimens obtained were naturally carbonized at 20 °C under 60 $\pm$ 5% relative humidity for 6 months before being tested.

FOOTNOTES

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REFERENCES

1 Davey, N. *A History of Building Materials*; Phoenix House: London, 1961; pp 97–98.

2 Woolley, L. *Excavations at Ur*; Ernest Ben: London, 1955; pp 22.

3 Moropoulou, A.; Bakolas, A.; Anagnostopoulou, S. Composite Materials in Ancient Structures. *Cem. Concr. Compos.* **2005**, *27*, 295–300.

4 Cowan, H. J. *The Master Builders: A History of Structural and Environmental Design from Ancient Egypt to the Nineteenth Century*; John Willey & Sons: New York, 1977.

5 Riccardia, M. P.; Duminucob, P.; Tomasic, C. Thermal, Microscopic and X-ray Diffraction Studies on Some Ancient Mortars. *Thermochim. Acta* **1998**, *321*, 207–214.

6 Böke, H.; Akkurt, S.; I$$İpekoğlu, B.; Uğurlu, E. Characteristics of Brick Used as Aggregate in Historic Brick-Lime Mortars and Plasters. *Cem. Concr. Res.* **2006**, *36*, 1115–1122.

7 Güleç, A.; Tulun, T. Physico-Chemical and Petrographical Studies of Old Motars and Plasters of Anatolia. *Cem. Concr. Res.* **1997**, *27* (2), 227–234.

8 Qiu, S. H. When Did the Lime Production Begin? The ^{14}C Isotopic Geochemical Method Can Answer the Question. *Archeology of Cultural Relics* **1980**, *5*, 126–130.

9 Wang, K. *The Ancient History of Road Transportation in Shanxi, China*; Communication Press: Beijing, 1989; pp 10.

10 Tie, F. D. Conservation and Restoration of Wall Paintings of Early Western Han Dynasty. *Sci. Conserv. Archaeol.* **2004**, *16* (1), 47–51.

11 Shen, K. *The Dream Rivulet Diary*; Times Wenyi Press: Changchun, China, 2001; pp 110.

12 Song, Y. Y. *Tian Gong Kai Wu*; Commercial Press: Shanghai, 1958; pp 197.

13 Li, X. H.; De, Q. S. The Artistic Appreciation of Stone Tower with Sutra Inscriptions. *Architect Gard* **2005**, *3*, 32–34.

14 Archeology Crew of Henan Province. *A Brick Tomb with Colorized Portrait in Deng country, Henan provice*; Cultural Relic Press: Beijing, 1958; pp 20.

15 Wu, Q. Z. The Experience and Implication for the Flooding Control in the Ancient Towns in China. *City Planning Review* **2002**, *26* (5), 76–84.

16 Yang, G. L. Viewing the Remains: Antirot Technique in the Ancient Grave Custom. *J. Changsha Soc. Work Coll.* **2004**, *4*, 11–15.

17 Nanjing Museum. The Tomb of Xupu and His Wife. *Cultural Relics* **1982**, *2*, 28–33.

18 Lin, J. S.; Lin, Z. J.; Chen, J. F. The Ancient Earthquake and Earthquake-Resistance of the Ancient Buildings in Quanzhou City. *World Earthquake Eng.* **2005**, *21* (2), 159–166.

19 Zhang, Y. H. *The History of Building Technology in Ancient China*; Science Press: Beijing, 1985; pp 173.

20 Wang, Y. M. *The Developing History of Cement in China*; China Architecture & Building Press: Beijing, 2005; pp 4–5.

21 Yang, T.; Zhou, J.; Zhou, C. Analysis and design of timeber-pile composite foundation on soft soils. *Chin. J. Rock Mech. Eng.* **2003**, *22* (9), 1560–1565.

22 Li, X. H. Research on the Protection and Repair of Main Structure for Mingyuan Bridge. *Build. Sci.* **2009**, *25* (4), 61–66.

23 Song, J. A Cultural Survey of the Old Bridges in Wudang Mountains Built in the Ming Dynasty. *J. Hubei Univ.* **2006**, *33* (5), 587–590.

24 Zhang, F. H.; Qiang, Y.; Du, F. D. Watchtower-like dwelling in Kaiping County. *Archit. J.* **2004**, *7*, 82–84.

25 Cai, J. S. Environment Friendly Castle-Like Dwellings. *Archit. J.* **1995**, *5*, 42–44.

26 Zhang, N. A. The Report about the Measurement Results of the Nanjing City Wall. Nanjing culture and culture relics Bureau, 2006.

27 Pavlovic, S.; Brandao, P. R. G. Adsorption of Starch, Amylose, Amylopectin and Alucose Monomer and Their Effect on the Flotation of Hematite and Quartz. *Miner. Eng.* **2003**, *16*, 1117–1122.

28 Rundl, R. E.; Foster, E. J. F.; Baldwin, R. R. On the Nature of the Starch–Iodine Complex. *J. Am. Chem. Soc.* **1944**, *66*, 2116–2120.

29 Genestar, C.; Pons, C.; Más, A. Analytical Characterisation of Ancient Mortars from the Archaeological Roman city of Pollentia. *Anal. Chim. Acta* **2006**, *557*, 373–379.

30 Liu, X. X.; Yu, L.; Liu, S. H.; Chen, L.; Li, L. Thermal Decomposition of Corn Starch with Different Amylose/Amylopectin Ratios in Open and Sealed Systems. *Cereal Chem.* **2009**, *86* (4), 383–385.

31 Chen, J. L. *The Researching About the Relation of Materials Prescription of Ancient Mortar and Strength*; National Cheng Kung University: Tainan, Taiwan, 2004, pp 14.

32 Zeng, Y. Y.; Zhang, B. J.; Liang, X. L. A Case Study and Mechanism Investigation of Typical Mortars used on Ancient Architecture in China. *Thermochim. Acta* **2008**, *473* (1–2), 1–6.

33 Yang, F. W.; Zhang, B. J.; Pan, C. C.; Zeng, Y. Y. Traditional Mortar Represented by Sticky Rice-Lime Mortar. *Sci. China, Ser. E: Technol. Sci.* **2009**, *52* (6), 1641–1647.

34 Yang, L.; Zhang, X. Y.; Liao, Z. J.; Guo, Y. M.; Hu, Z. G.; Cao, Y. Interfacial Molecular Recognition between Polysaccharides and Calcium Carbonate during Crystallization. *J. Inorg. Biochem.* **2003**, *97*, 377–383.

35 Steven, R. D.; McGrath, K. M. Aqueous Precipitation of Calcium Carbonate Modified by Hydroxyl-Containing Compounds. *Cryst. Growth Des.* **2004**, *4* (6), 1141–1148.

36 Vishwas, V.; Hardikar, I.; Egon, M. Influence of Ionic and Nonionic Dextrans on the Formation of Calcium Hydroxide and Calcium Carbonate Particles. *Colloids Surf., A* **2001**, *186*, 23–31.

37 Standard for Test Method of Performance on Building Mortar (JGJ/T70-2009).

38 Pavía, S.; Fitzgerald, B.; Howard, R. *Evaluation of Properties of Magnesian Lime Mortar*; WIT Press: Southampton, U.K., 2005; pp 375–384.

39 Specification for Mix Proportion Design of Masonry Mortar (JGJ/98-2000).

40 Leemann, A.; Winnefeld, F. The Effect of Viscosity Modifying Agents on Mortar and Concrete. *Cem. Concr. Compos.* **2007**, *29*, 341–349.

41 Sjöqvist, M.; Gatenholm, P. The Effect of Starch Composition on Structure of Foams Prepared by Microwave Treatment. *J. Polym. Environ.* **2005**, *13* (1), 29–37.

42 Van Balen, K.; Van Gemert, D. Modelling Lime Mortar Carbonation. *Mater. Struct. (Bagneux, Fr.)* **1994**, *27*, 393–398.

43 Michoinová, D.; Rovnaníková, D. High-Calcium Lime Mortar: The Effects of Traditional Preparation and Curing. *APT Bull.* **2008**, *39* (4), 23–29.

44 Chandra, S.; Eclund, F.; Villarreal, R. R. Use of Cactus in Mortars and Concrete Research. *Cem. Concr.* **1998**, *28*, 41–45.

45 DeSilva, P.; Bucea, L.; Moorehead, D. R.; Sirivivatnanon, V. Carbonate Binders: Reaction Kinetics, Strength and Microstructure. *Cem. Concr. Compos.* **2006**, *28*, 613–620.

46 Franco, M.; Rinaldi, G. Poly-Amino-Phenolic Additives Accelerating the Carbonation of Hydrated Lime in Mortar. *Environ. Eng. Sci.* **2002**, *19* (4), 271–276.

47 Bostenaru-Dan, M. *Materials, Technologies and Practice in Historic Heritage Structures*; Springer: Dordrecht, The Netherlands, 2010; pp 37.

48 Standard for Test Method of Performance on Building Mortar (JGJ/70-1990)

49 Methods of test for mortar for masonry—Part 19: Determination of Water Vapor Permeability of Hardened Rendering and Plastering Mortars (BS EN 1015-19:1999).

50 Ziad, A. S.; Mohamed, A. H. Laboratory Evaluation of Various Types of Mortars for the Conservation of Qasr al-Bint monument, Petra, Jordan. *Eng. Struct.* **2001**, *23*, 926–933.

51 Fernández-Muñoz, J. L.; Zelaya-Angel, O.; Cruz-Orea, A.; Sánchez-Sinencio, F. Phase Transitions in Amylose and Amylopectin Under the Influence of $Ca(OH)_2$ in Aqueous Solution. *Anal. Sci.* **2001**, *17*, 338–341.

52 Watta, D.; Colston, B. Investigating the Effects of Humidity and Salt Crystallization on Medieval Masonry. *Build. Environ.* **2000**, *35*, 737–749.

53 Methods of test for mortar for masonry—Part 21: Determination of the Compatibility of One-Coat Rendering Mortars with Substrates (BS EN1015-21:2002).