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Comparison in Chemical Composition of Lime Binders between Several Typical Ancient Buildings in China

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Abstract. This paper aims to compare the chemical and phase compositions of lime binders in ancient buildings. To this end, X-ray diffractometer (XRD) and FT-IR testing were used to analyse the representative samples by sampling the lime-based binding materials of several typical ancient buildings in China. The test results showed that the lime binder contained residual glutinous rice amylopectin; just because of this inorganic and organic synergistic effect of glutinous rice and lime can the lime binders have excellent properties. This provides a theoretical basis for the subsequent study.

1. Introduction

In China's ancient buildings, the lime-based binders were used for a long period. With the progress of history, such binding material gradually evolves from the original single-component mortar into a complex system containing multiple components [1, 2]. It has been found that China started to use an organic-inorganic composite material long before, that is, a traditional Chinese lime mortar combining the inorganic materials such as lime and the organic materials such as glutinous rice etc [3, 4]. Using modern technology to explore the physical properties, chemical and phase composition, and ingredient proportion of this organic-inorganic composite lime binder, as well as the interaction mechanism between key components can not only promote Chinese culture, but also absorb and utilize the advantages of traditional technology for current use. In particular, it is of great practical significance for guiding and promoting the protection of ancient buildings in the future [5, 6]. Therefore, taking the lime binder materials of several ancient architectural sites as samples, this paper analyses the chemical composition of the representative samples by X-ray diffractometry (XRD) and FT-IR test, which provides a theoretical basis for the subsequent study.

2. Test of Ancient Lime Samples

2.1. Sampling Location

According to archaeological records, when the Great Wall was built in Qin Dynasty, people learned to use a composite binding material composed of glutinous rice and lime.; in the northern and southern dynasties, a composite material containing starch was added to the lime; in the Ming Dynasty, the glutinous rice-lime composite binder was the most frequently used. In this study, nine ancient architectural buildings were sampled, from the Ming Dynasty to the Qing Dynasty. Table 1.1 lists the sample information.

Table 1. The Sample Information

Sample	Sample source	Date
#1	The Gate of China, Nanjing City	1369-1375 CE (Ming dynasty)
#2	Ming Tomb, Nanjing City	1381-1405 CE (Ming dynasty)
#3	Scholar Zhu lane, Nanjing City	1573-1620 CE (Ming dynasty)
#4	Tunxi Old Street, Huangshan City	Before 1548 CE (Ming dynasty)
#5	YangliuVillage, Nanjing City	1579 CE (Qing dynasty)
#6	Zhangtan, Huangshan City	1832 CE (Qing dynasty)
#7	Zhouzhuang Town, Suzhou City	1720 CE (Qing dynasty)
#8	Hongcun Town, Huangshan City	Before 1620 CE (Qing dynasty)
#9	Yu Garden, Nanjing City JinXi	1876 CE (Qing dynasty)

2.2. *Test Methods*

After crushing each sample, some small pieces in size 2.5mm-5.0mm were taken. Then, removing the sandstone contained, they were ground to less than 0.08mm in an agate mortar, and dried at 40 ℃ for 24 hours. Next, the dried samples were kept in the dryer for XRD and FT-IR testing.

3. Results and Discussion

3.1. *XRD Analysis*

Figure 1 shows the XRD pattern of the lime binder samples. It can be seen from the XRD line that a main peak appeared at a 2θ angle close to 30°, which corresponded to a characteristic peak of calcium carbonate in the calcite crystal form. In addition, in the 3#, 4#, 8#, and 9# samples, another significant main peak appeared at a 2θ angle of approximately 27°, which corresponded to a characteristic peak of the quartz crystal form. Also, the XRD pattern analysis found that the main components of the 1#, 2#, 5#, 6#, and 7# samples were calcite crystal calcium carbonate in which a small amount of clay mineral was doped, while the 3#, 4#, 8#, and 9# samples contained not only calcite crystal calcium carbonate, but also the significant characteristic peaks of quartz crystal form, which indicates that these four samples are mainly composed of lime and clay, similar to the described trinity mixture fill in the relevant literature.

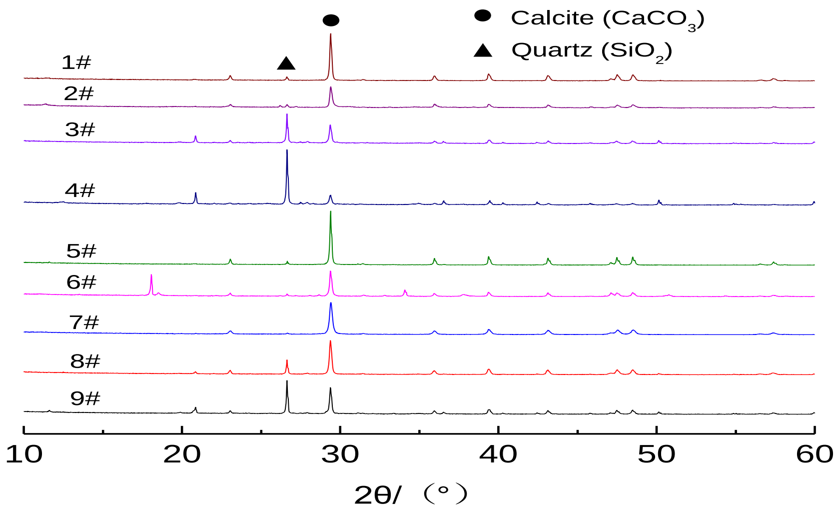

Figure 1. XRD Patterns of Lime Binders

3.2. *FT-IR Analysis*

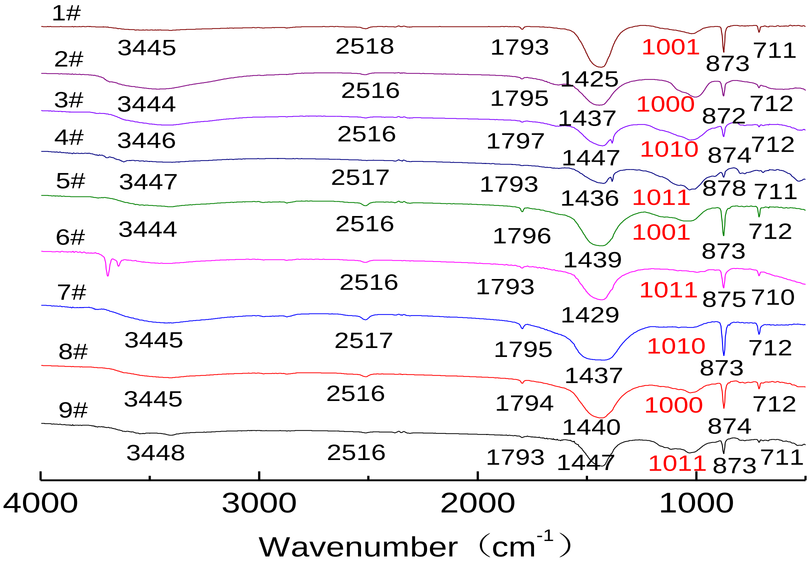

Figure 2. FT-IR Patterns of Lime Binders

Figure 2 shows the results of the FT-IR test. It can be seen from the figure that the absorption peaks near the wavenumbers of 712, 876, 1429, 1794, and 2513 cm-1 were attributed to the characteristic peak of calcite, so it can be inferred that the calcium carbonate contained in samples mainly used a calcite crystal form; also, the absorption peak (a.1000cm-1, c.1010cm-1, d.1011cm-1) near wavenumber 1018cm-1 corresponded to the characteristic peak of a constituent polysaccharide compound in the amylopectin of glutinous rice, which is caused by stretching vibration of a large number of C-O(H) groups [130]. Through the relative intensity of the main strong peak of amylopectin, rapid mass identification can be carried out to determine the amount of amylopectin added in different representative samples. Among them, the amount of amylopectin added in samples 2#, 3# and 4# was the most, followed by the samples 8#, 9#, and samples 6#, 7# had the least proportion of amylopectin.

3.3. *Mechanism Explanation*

Studies have shown that as a key component in traditional mortars, glutinous rice and lime play a major role in improving the bond strength of mortar, while soil and sand are inert components, and they basically function only as fillers. Besides, glutinous rice has a regulating effect on the carbonation of lime. Glutinous rice is a kind of polysaccharide matter. Modern scientific research shows that bio-polysaccharides can often be used as a template agent for biomineralization process to constrain and regulate the size, morphology and structure of crystalline particles formed by inorganic ions during crystallization. Therefore, added with this agent-glutinous rice, the calcium carbonate formed by the mineralization reaction of Ca(OH)2 solution is a nanometre-scale fine particle of calcite crystal form, which is much finer and denser than that without glutinous rice. This fine structure can greatly improve the compressive strength and surface hardness of the mortar.

4. Conclusions

The hardening process of the quicklime mortar involving the glutinous rice is actually the biomineralization process of calcium carbonate added with the natural bio-polysaccharide (glutinous rice). In this process, glutinous rice not only plays a role in regulating the crystallization process and microstructure of calcium carbonate, but also closely combines with the generated calcium carbonate to form a composite structure in which organic matter and inorganic matter are combined and densely filled. This should be the microscopic basis for excellent mechanical properties of glutinous rice such as high mortar strength and toughness.

5. Acknowledgements
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6. References
[1] Wang X, Lam C C, Iu V P, Experimental investigation of in-plane shear behaviour of grey clay brick masonry panels strengthened with SRG, Eng. Struct. 162 (2018) 84-96.
[2] Pan G G, A History of Chinese Architecture (in chinese), China Architecture & Building Press, Beijing, 2004.
[3] Liu Y, Brief Excavation Report of the Eastern Zhou Dynasty Rouyou site in Shanxi province (in chinese), Archaeol. Rel. 31(1991) 9-10.
[4] Shan C R, The report on archaeological excavations of the Chenhan tomb site in Shanxi province (in chinese), Shanxi people's publishing house, Shanxi, 2006.
[5] Shen Y, The study of ancient Chinese eaves tiles (in chinese), Cultural relics publishing house, Shanxi, 2006.
[6] Wu J, Wu J H, Wang H S, Lu X K, Wu J M, The technical research on the huge glazed brick from the relic of Nanyue Kingdom Palace, Sci. China. Ser. E. 51(1) (2008) 16-24.