Degradation assessment of waterlogged wood at Haimenkou site

Gao Jingran, Li Jian
Northeast Forestry University Material Science and Engineering institute, Ha'erbin, Heilongjiang 150040
E-mail:48682171@qq.com

Qiu Jian
Southwest Forestry University School of materials engineering, Kunming, Yunnan 650024
E-mail:qiujianswfu@foxmail.com

Guo Menglin
Iowa State University, Iowa, U.S.A)

ABSTRACT. Haimenkou site is the largest railing-enclosed wooden architecture settlement site on the waterfront in current China. This research conducts degradation assessment of waterlogged wood at Haimenkou site with various methods, including maximum moisture content analysis, basic density analysis, shrinkage measurement, swelling analysis, chemical composition analysis, measurement of compression strength parallel to grain, SEM microstructure analysis and measurement of crystallinity, providing scientific guidance for the subsequent formulation of proper methods of reinforcement.

KEYWORDS. Haimenkou site; Waterlogged wood; Degradation assessment.

INTRODUCTION

Haimenkou site locates at 1 km northwest to Haimenkou village in Diannan, Jianchuan, Dali, Yunnan province, whose GPS coordinates are 99°33´~100°33´ E and 26°12´~26°41´ N, adjoining the northwest bank of Haiwei River at the southwest outfall of Jian lake. During the archaeological excavation, a huge area of wooden architecture relics and abundant cultural relics such as pottery, bronze ware, stoneware and ironware were discovered. C14 analysis shows they could be dated back to 5300~2500 years ago, counted as a Neolithic or Bronze-age settlement site. Since 1957 the site has been unearthed for three times, the third one in 2008 excavating more than 4000 timber piles in an excavation unit of 1395 square meters. Meanwhile, the site area was measured to be 140000 m^2, and the concentration area of timber piles was measured as 20000-25000 m^2, making it the largest railing-enclosed wooden architecture settlement site on the waterfront in current China. Its rareness on earth provides a precious case for analyzing types of Chinese prehistoric settlements, and is of great value on the study of social development history and ethnic history of Yunnan Province.

Professor Qiujian from Southwest Forestry University has conducted random sampling test on unearthed wood piles, finding most of the tree belonged to Pinus yunnanensis. Therefore this research chooses waterlogged wood Pinus yunnanensis as samples to develop degradation assessment, trying to provide scientific guidance for the subsequent formulation of proper methods of reinforcement.

MATERIALS AND METHODS

Specimen Source

Waterlogged wood is collected from test pit AT2001 of Haimenkou site with a diameter of 12.7cm, length of 62cm and weight of 7.9kg. It belongs to the middle period, and the species belongs to Pinus yunnanensis (Pinus yunnanensis).

Due to the severe degradation, the waterlogged wood is as soft as sponges, which requires the PEG- embedding before sawing the specifications sample. The preparation method was the following:

- soak the ancient wood in PEG2000 at 60°C. After 15 days, when the ancient wood is totally immersed in PEG;
- dry it in the air and leave it to harden;
- Saw the specimen into needed sizes, and put it in water to draw out PEG for 10 days (each day replace clean water).

The contrast sample, Pinus yunnanensis (Pinus yunnanensis) healthy wood, is collected from Puer, Yunnan.

Experimental methods: Maximum moisture content and basic density

Maximum moisture content is measured according to GB/T1931-2009 Method for Determination of the Moisture Content of Wood. To ensure the maximum moisture content of wood during measurement, the saturation of wood with water is needed:

- put the sample into a vessel with distilled water;
- immerse it totally into water by a stainless steel wire mesh;
- leave the vessel to a vacuum drying oven for 1 hour to vacuumize with the vacuum degree of -0.09 MPa;
- release the vacuum and still the sample;
- conduct measurement after the sample weight becomes stable.

Basic density is tested according to GB/T1933-2009 Method for Determination of the Density of Wood, Chapter 7.

Experimental methods: Shrinkage, swelling and water absorption

Shrinkage is measured according to GB/T1932-2009 Method for Determination of the Shrinkage of Wood; swelling is determined according to GB/T1934.2-2009 Method for Determination of the Swelling of Wood; water absorption is determined according to GB/T1934.1-2009 Method for Determination of the Water Absorption.

Experimental methods: Compressive strength parallel to grain of wood

The compressive strength parallel to grain of wood is measured according to GB/T1935-2009 Method of Testing in Compressive Strength Parallel to Grain of Wood.

Experimental methods: Chemical composition analysis

The content of solvent extractives is measured according to GB/T2677.6-94 Fibrous Raw Material—Determination of Solvent Extractives. The content of acid-insoluble lignin is measured according to Fibrous Raw Material—Determination of Acid-insoluble Lignin. The content of holocellulose is measured according to GB/T2677.10-94 Fibrous Raw Material-Determination of Holocellulose. The content of pentosan is measured according to GB/T2677.9-94 Fibrous Raw Material—Determination of Pentosan.

Experimental methods: Scanning electron microscope (SEM) examination

The scanning electron microscope is Hitachi S-3000N, whose accelerating voltage is 15.0kV. The sample is cut by hand from horizontal, radial and chordwise sections using Germany Leica specialized microtome blade.

RESULTS AND DISCUSSION

Maximum moisture content and basic density

As is shown in Tab. 1, maximum moisture content and basic density are two scientific and relatively more easily-operated indicators for the degradation degree of waterlogged wood [1]. Waterlogged wood is usually divided into 3 categories according to its preservation states:

- Category I, maximum moisture content ≥400%, severe degradation;

- Category II, 400% > maximum moisture content >185%, moderate degradation;
- Category III, maximum moisture content ≤185%, mild degradation [2].

Within the same species, the further the waterlogged wood basic density is away from that of healthy wood, the more severe its degradation is. During the reinforcement, if there appears an obvious tendency of cell collapse and dimension shrinkage [3], then milder methods is supposed to be chosen in the later drying process. As is shown in Tab. 1, the maximum moisture content of ancient wood is 578.68%, 4.14 times of the healthy wood (139.64%), while the basic density of waterlogged wood (0.16 g/cm^3) is only one-third of that of healthy wood (0.48 g/cm^3), indicating that Haimenkou site waterlogged wood has a severe degradation.

		sample size	mean/%	max/%	min/%	standard deviation	variable coefficient/%
basic density g/cm^3	ancient wood	60	0.16	0.22	0.13	0.02	14.51
	modern healthy wood	60	0.48	0.58	0.36	0.06	12.24
maximum saturation moisture content %	ancient wood	60	578.68	705.92	373.52	66.58	11.51
	modern healthy wood	60	139.64	190.75	102.08	24.91	17.84

Table 1: Maximum moisture content, basic density and oven dry porosity of Pinus yunnanensisancient wood and healthy wood.

Shrinkage, swelling and water absorption

The rules of shrinkage and swelling of waterlogged wood are different from healthy wood. Tab. 2 shows the following conclusions:

1) The shrinkage rate of waterlogged wood from waterlogged state to full hardness (radial direction 8.16%, chordwise 24.74%) is obviously higher than healthy wood (radial direction 4.46%, chordwise7.76%), indicating that Haimenkou site ancient wood has severe shrinkage. In the drying process during late reinforcement, the removal of solvent should slow down, preventing the deformation and craze of the ancient wood caused by cell collapse.
2) The swelling of waterlogged wood from full hardness to waterlogged state (radial direction 4.12%, chordwise11.28%) is slightly higher than healthy wood (radial direction 4.46%, chordwise8.50%). Besides, the swelling of waterlogged wood is much lower than its shrinkage, meaning that the re-absorption of water after drying process cannot return to the original size, though it can swell to a certain extent. According to previous studies, the more severe degradation of waterlogged wood is, the larger disparity there will be. Repeated drying and swelling of ancient wood will lead to larger and larger disparity [4]. The reason lies in the degradation of polysaccharide substances in ancient wood, which produces large amount of hydroxyl and increases porosity of wood, leading to the increase of ancient wood maximum saturation moisture content. In the drying process, as water is drawing out, cellulose chains are growing closer, allowing hydroxyl to form hydrogen bond. When the ancient wood after oven dry reabsorbs water, the newly formed hydrogen bonds can no more accept water molecules, making the swelling unable to return to original size.
3) The shrinkage of healthy wood chordwise is 1.74 times that of radial direction, while the shrinkage of waterlogged wood chordwise is 3.03 times that of radial direction. The result demonstrates that compared with healthy wood, there is a larger gap between the shrinkage of waterlogged wood from chordwise and radial direction. The main reason lies in the containment of wood ray, which is the major difference between the woods from radial direction and chordwise. For waterlogged wood whose cytoderm is severely degraded, the containment of wood ray is more obvious.
4) Water absorption of full hardness waterlogged wood (454.29%) is much higher than that of healthy wood (144.97%).

Compression strength parallel to grain

As Tab. 3 shows, the compression strength parallel to grain of Pinus yunnanensis healthy wood is 59.28 MPa while that of Pinus yunnanensis ancient wood is only 3.67 MPa, indicating the mechanical strength of ancient wood in Haimeikou site is unable to support its exhibition, storage and transport as wood relics. Therefore the timely reinforcement is needed. Besides, the maximum indenter displacement of cracking load of ancient wood (1.30 mm) is lower than that of healthy wood (1.52 mm), showing that elasticity of ancient wood after air-seasoning is lower than healthy wood, indicating higher brittleness which is adverse to the preservation of ancient wood.

Analysis of causes for the heavy decrease of compression strength parallel to grain of Haimenkou site waterlogged wood can be summarized as follows:

1) from macro-perspective, severe degradation leads to the shrinkage distortion of ancient wood in the process of air-seasoning. Shrinkage cracks appear in part of the wood, some of which has a sharp fall of the compression strength parallel to grain, one of the reasons for the significant excess of ancient wood variable coefficient than healthy wood.
2) from micro-perspective, degradation of three major chemical dispositions in wood causes destruction of cytoderm, increase of porosity and decrease of crystallinity, which all contribute to the fall of compression strength parallel to grain in ancient wood.
3) from molecule perspective, degradation and breakage of cellulose chain impairs its original rigidity. Degradation of hemicelluloses and lignin reduces the closeness between cytoderm matrix substances.

			sample size	mean/%	max/%	min/%	standard deviation	variable coefficient/%
Shrinkage from saturation to full hardness /%	radial direction	waterlogged wood	60	8.16	13.41	3.84	2.19	26.88
		modern healthy wood	60	4.46	6.90	2.56	1.20	26.98
	chordwise	waterlogged wood	60	24.74	32.16	7.20	6.13	24.78
		modern healthy wood	60	7.76	9.57	5.66	1.12	14.44
Swelling from full hardness to saturation /%	radial direction	waterlogged wood	60	4.12	6.01	2.06	1.06	25.79
		modern healthy wood	60	4.46	6.69	2.59	1.14	25.51
	chordwise	waterlogged wood	60	11.28	16.91	6.65	2.58	22.89
		modern healthy wood	60	8.50	10.75	6.24	1.32	15.59
Water absorption from full hardness to saturation /%		waterlogged wood	60	454.29	584.63	337.96	60.00	13.21
		modern healthy wood	60	144.97	212.74	104.94	27.24	18.79

Table 2: Shrinkage, swelling and water absorption of Pinus yunnanensis ancient wood and healthy wood.

		sample size	moisture content/%	mean	max	min	standard deviation	variable coefficient/%
moisture content is 12% /MPa	waterlogged wood	26	12.09	3.67	4.93	1.98	0.76	20.73
	modern healthy wood	26	10.99	59.28	68.85	49.57	5.42	9.15
the maximum indenter displacement of cracking load /mm	waterlogged wood	26	12.09	1.30	2.03	0.96	0.26	19.94
	modern healthy wood	26	10.99	1.52	2.23	1.21	0.25	16.38

Table 3: compression strength parallel to grain of Pinus yunnanensis ancient wood and healthy wood.

Chemical components of waterlogged wood

For ancient wood, the content of extractions can to some extent demonstrate its environment and degradation degree. As is shown in Tab. 4, the content of 1%NaOH extraction of waterlogged wood (12.85%) is much higher than modern healthy wood (7.38%). It's because Haimenkou site ancient wood has been buried under oxygen-deficient and high temperature environment all year round, under which ancient wood is mainly corrupted by anaerobic bacteria. Most of the compositions degraded by anaerobic bacteria are celluloses and hemicelluloses. Hemicelluloses in ancient wood are degraded into glycosyl units such as hexose and pentosan with the impact of light, heat, oxidation and microorganism. The glycosyl units can be extracted by 1%NaOH solution, causing the content of 1%NaOH extraction in ancient wood higher than healthy wood. The research shows a positive correlation between severities of degradation of ancient wood and the relative extraction content of 1%NaOH solution in ancient wood compared with healthy wood [5].

The content of holocellulose can relatively be more accurate in reflecting the rotten degree of waterlogged wood [6-8]. The white rot fungi, which can degrade lignin, belong to aerobic fungi. Therefore in oxygen-deficient environment the lignin cannot easily be degraded. According to previous studies, the degradation of ancient wood mainly includes the degradation of celluloses and hemicelluloses. As is shown in Tab. 4, the content of holocellulose in ancient wood is 42.94%, taking up only 55% of that in healthy wood (78.38%). The low content of holocellulose indicates that celluloses and hemicelluloses have been severely degraded.

The content of pentosan in ancient wood is 2.91%, only 22% that of healthy wood (13.23%), showing that the degradation of hemicelluloses is more serious than celluloses. The reason is that although celluloses and hemicelluloses are both high-molecular polymer made up by glycosyl units, celluloses have no branched chain, and possess only one kind of glycosyl, while hemicelluloses are made up by various kinds of glycosyl and have many short branched chains[9], making it easier for hemicelluloses to be degraded.

As is shown in Tab. 4, the content of lignin in ancient wood is 57.99%, while in healthy wood the figure is 30.48%. Superficially the lignin content has increased, but it is a relative increase caused by a larger decrease of celluloses and hemicelluloses.

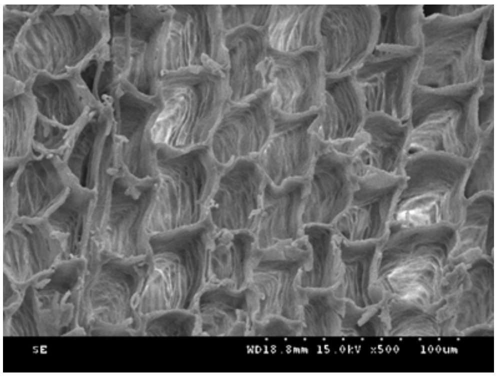
	alcohol-benzene extract /%	1%NaOH extract/%	acid accumulator insoluble lignin /%	holocellulose /%	pentosan /%
waterlogged wood	2.16	12.85	57.99	42.94	2.91
healthy wood	2.35	7.38	30.48	78.38	13.23

Table 4: Chemical compositions of Pinus yunnanensis ancient wood and healthy wood.

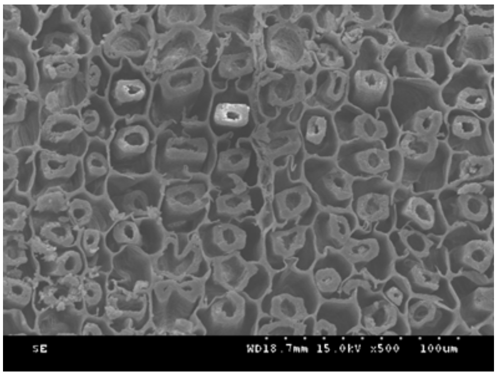
Scanning electron microscope (SEM) examination of ancient wood

Seen from Fig. 1(a), the cytoderm of early wood cells on cross section of waterlogged wood at Haimenkou cannot keep original forms due to the degradation of chemical compositions such as celluloses. Fig. 1 (b) shows that the latewood secondary wall of ancient wood cross section is seriously degraded and shrank, breaking away from the relatively well-preserved middle lamella. SEM samples of ancient wood are selected from natural drying waterlogged wood. Natural drying can cause serious shrinkage and deformation of ancient wood cells, demonstrating that the wood cells must be padded and consolidated with reagent to maintain the state of ancient wood before dehydration.

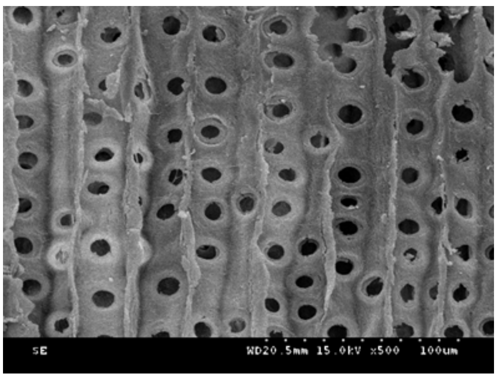
Fig. 1 (c) shows that the diameter of cytoderm pit on radial section of ancient wood is long and in large quantity, whose pit membrane has been destroyed. The permeability of wood is closely related to the number and radius of pit membrane micropores, which offers a favorable condition for the entry of reinforcement reagent inside the cytoderm of ancient wood cells. It is predicted that no inflating or vacuum is needed during the reinforcement process but ordinary pressure. In this way it not only prevents fragile wood cells from high pressure, but also reduces the cost and time.



(a) 500×waterlogged wood SEM microstructure of early wood cells on cross section



(b) 500×waterlogged wood SEM microstructure of late wood on cross section



(c) SEM microstructure on radial section of 500×waterlogged wood.

Figure 1: Waterlogged wood SEM microstructure.

CONCLUSION

1) The maximum moisture content of unearthed waterlogged wood at Haimenkou site is 578.68%, its basic density is 0.16g/cm^3, full hardness shrinkage on radial direction is 8.16% and chordwise 24.74%, largely different from healthy wood.
2) The compression strength parallel to grain is 3.67 MPa, only 6.19% of the healthy wood, unable to support the sequent exhibition and preservation. The timely reinforcement is needed.
3) The degradation of celluloses and hemicelluloses in waterlogged wood at Haimenkou site is serious, which is the major cause for the degradation of ancient wood's physical and mechanical performance.
4) According to the analysis on full hardness shrinkage and SEM microstructure, the waterlogged wood cells endure severe shrinkage and deformation in the natural drying process, which further leads to the cracking of the wood. Therefore special attention should be paid to adopting mild drying methods in drying and reinforcement process.

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