Investigation for Degraded Stone Pillar Bases of the East Cocoon Warehouse of the Tomioka Silk Mill By X-Ray Diffraction Analysis

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ABSTRACT

In 2014, "Tomioka Silk Mill and Related Sites" was inscribed on the World Heritage list for which have bear witness to the renewal of sericulture and industrialisation of Japan and the development of international raw silk industry in the early 20th century. As the main constitute of this heritage, the Tomioka Silk Mill, which locates in Tomioka City, Gunma Prefecture, is now open to the public.

Along with converting from industrial spaces into public spaces, degradations of constitutions of the Tomioka Silk Mill, (e.g., bricks, timber frames, stone pillar bases) have been observed. In the Eastern Cocoon Warehouse, which is utilised as exhibition space in recent years, salt precipitations and powdering phenomenon on the surface of stone pillar bases is threatening the long-term preservation of the historic building itself. In order to figure out the relevant factors that have induced these degradations, and develop a suitable conservation method, surface precipitations and powders of 88 stone pillar bases of the Eastern Cocoon Warehouse have been investigated.

The stone base samples have been analysed by X-ray diffraction analysis(XRD).In XRD analysis result, except for mineral constituents of stone (e.g., orthoclase, quartz, kaolinite, etc.), calcium and magnesium sulfates (gypsum, hexahydrite, etc.) also have been detected mainly in samples from exterior stone bases. The formation of sulfate minerals is possible due to a chemical process between carbonate constitutes in stone and SO_2, O_2 in surrounding atmosphere, or physical process induced by water activities between stone bases and earthen foundation of the building.

http://www.tomioka-silk.jp/tomioka-silk-mill/guide/id=736

Figure 1: The East Cocoon Warehouse of the Tomioka Silk Mill

1. INTRODUCTION

In 2014, “Tomioka Silk Mill and Related Sites” was inscribed on the World Heritage list for which have bear witness to the renewal of sericulture and industrialisation of Japan and the development of international raw silk industry in the early 20th century. As the main constitute of this heritage, the Tomioka Silk Mill, which locates in Tomioka City, Gunma Prefecture, is now open to the public.

Along with converting from industrial spaces into public spaces, degradations of constitutions of the Tomioka Silk Mill (e.g., bricks, timber frames, stone pillar bases) have been observed. In the East Cocoon Warehouse, which is utilised as exhibition space in recent years, salt precipitations and powdering phenomenon on the surface of stone pillar bases is threatening the long-term preservation of the historic building itself. In order to figure out the relevant factors that have induced these degradations, and develop a suitable conservation method, surface precipitations and powders of 88 stone pillar bases of the East Cocoon Warehouse have been collected and investigated (Including 60 of the exterior eastern and western sides, 4 of the exterior northern and southern sides, 24 in interior space).

2. METHOD

After being finely powdered in an agate mortar, the stone base samples have been analysed by X-ray diffraction analysis (XRD). XRD spectroscopy is an economic and reliable technique utilising the X-ray diffraction from periodic crystal lattices, to obtain X-ray diffraction spectrum for identifying and quantifying the crystalline phases in samples. XRD analysis measurements have been conducted with the Bruker AXS, D8 ADVANCE/TSM under conditions of 1.542 nm CuKα Radiation at 40mV/40mA, over 5° -70° 2θ interval, at a scanning speed of 0.1 sec/step (6000 steps in total).

3. RESULTS AND DISCUSSION

In most samples quartz, feldspars (identified as orthoclase in this study), clay minerals (kaolinite) are identified, which are considered as common components in stone. Besides, calcite, gypsum and hexahydrite($MgSO_4 \cdot 6H_2O$) are also identified in some samples.

The results of the X-ray diffraction analysis are summarized in Fig.2. In different side of the East Cocoon Warehouse, results of the X-ray diffraction analysis appear different characteristics.

In the case of the eastern exterior side, calcite ($CaCO_3$) are identified in samples of No.1~10, 13~17, 22 stone pillar bases, which are mainly located at north part of the eastern exterior side. On the other hand, the stone pillar bases from which gypsum($CaSO_4 \cdot 2H_2O$) are identified, are seems neighboring roof drain pipes(No. 6, 17, 18, 20, 23, 25, 30 stone pillar bases). In the sample of No. 23, the hexahydrite is detected along with gypsum.

In the case of the western exterior side, calcites are identified in several samples collected from No. 9, 13, 14, 18, 19, 25, 27. While in most samples, gypsums are identified (except for No.21, 25, 27 stone pillar base). In samples of No. 1~5, 7, 11, 12, 26, 28 the hexahydrite are detected along with gypsum.

In the case of the northern exterior side, gypsum is identified in samples of No. A. In the case of the southern exterior side, gypsum is detected along with hexahydrite in sample of No.C, gypsum IS detected along with calcite in sample of No.D.

In the case of the interior side, calcite are identified in No. 2~9, 12~21, 24 stone pillar bases, gypsum are identified in No.4, 10~13, 26 stone pillar bases. In the sample of No. 26, the hexahydrite is detected along with gypsum.

The precipitations of calcium and magnesium sulfates appear mainly in northwestern part of the East Cocoon Warehouse.

4. CONCLUSIONS

Although stone pillar bases of exterior side of the East Cocoon Warehouse appear to be sound and intact now, some precipitations identified in this investigations implies progressing degradations.

The calcite is a typical natural component of stone, migration of calcium and recrystallization of calcite on the surface of stone can be occurred in environment with high CO_2 levels. The porous recrystallized calcite makes the penetration of salts and pollutant gases become much easier.

The pollutant gas SO_2 is mostly considered responsible for formation of gypsum. The sulphuric acid (H_2SO_4) formed by oxidized SO_2 and water, can react with calcareous materials to form calcium sulfates. Besides, the sulfates members of the $MgSO_4 \cdot nH_2O$ series are also highly dangerous for stone as same as calcium. The transition of $CaSO_4$ and $CaSO_4 \cdot 2H_2O$, epsomite ($MgSO_4 \cdot 7H_2O$), hexahydrite ($MgSO_4 \cdot 6H_2O$) and kieserite ($MgSO_4 \cdot H_2O$), are reversible and highly depending on the humidity. The recycle of "obtaining and losing extra-polyhedral water progress" may lead to size changes of sulfate crystals, which will ultimately induce micro-crack and fragile of stone.

In the case of Tomioka Silk Mil, after being inscribed as word heritage in 2014, the visitors increased 3-fold than 2013 as 1,337,720. The great population of visitors will continue in future decades. Along with the vast rise in the number of visitors, the increase of pollutant gases level, oscillation vibration of temperature and humidity surrounding this heritage is definitely inevitable.

On the other hand, the salt degradation of stone is also highly correlated with water movements among the building and its earthen foundation, which is still unknown now.

Therefore, the continuous monitoring of gaseous pollutants, temperature and humidity, and water movement in building earthen foundation is now conducted in the East Cocoon Warehouse. The accumulated data will be analyzed in the future for making visitor management measurements and improving water drainage system.

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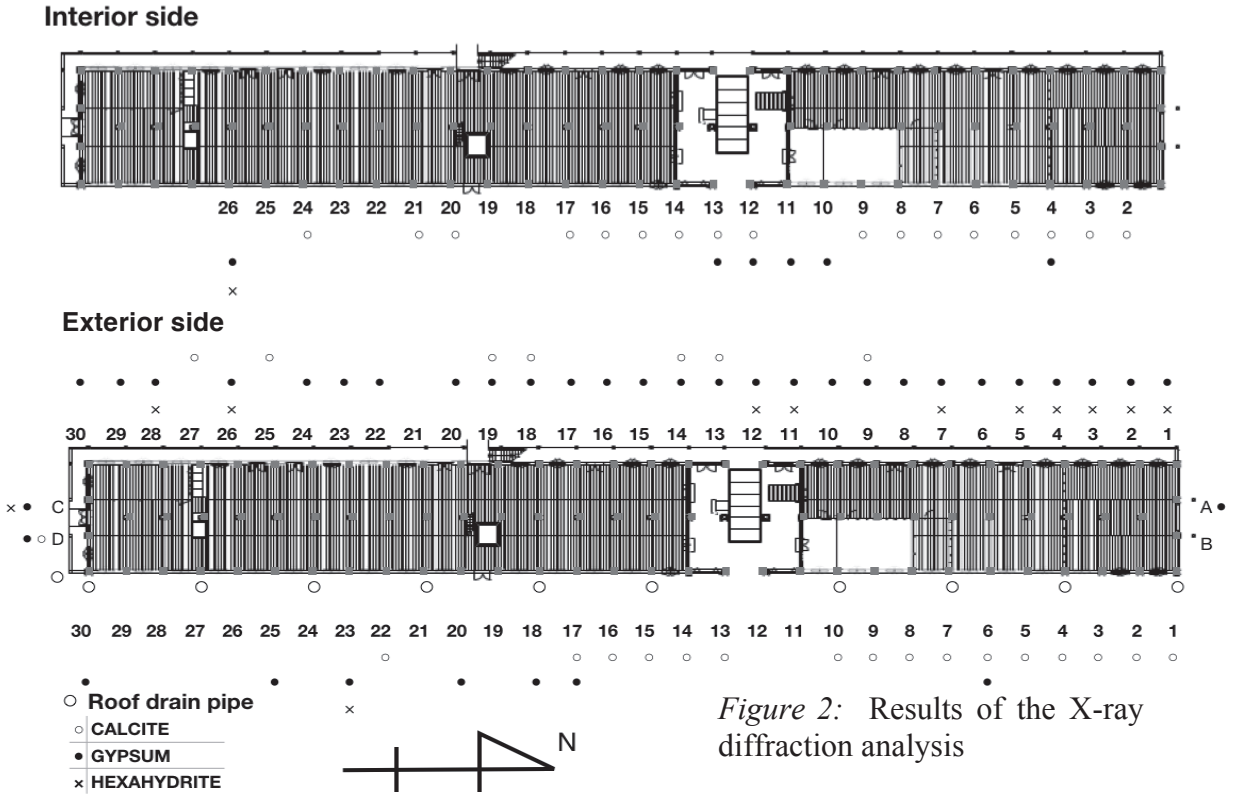

Figure 2: Results of the X-ray diffraction analysis

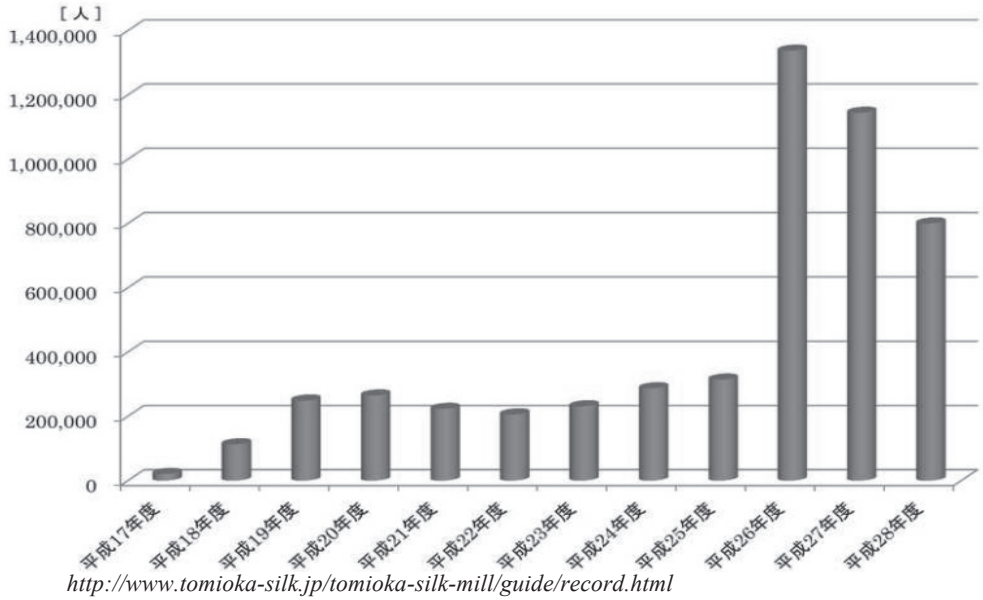

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Figure 3: Population changes of visitors in the Tomioka Silk Mill