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Characterization of "Stalactite" Hanging from Old Concrete Bridge

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Stalactitic rods (city stalactites) taken from an old concrete bridge built in 1970s were characterized. Every rod had a straw-like hollow. The hollow opened at the front of the rod, which differs from natural stalactites with closed conical fronts. The inside wall of the hollow was constructed of almost colorless and transparent angular grains. The growth rate of the city stalactites was ca. 7.5mm/y that is very faster than that of ca. 0.25 mm/y of natural stalactite. Such a fast growth rate of the city stalactites suggested an easy dissolution of concrete constituents in rainwater. The mineral phase of the city stalactites was pure calcite-type $CaCO_3$. Impurities in the city stalactites were not detected by EDX.

Keywords: City stalactite, Calcium carbonate, Stalactite

1. INTRODUCTION

In recent years, stalactitic rods (hereafter, city stalactites) hanging from old concrete bridges have been often observed in cities. In natural stalactite caves, firstly calcium carbonate ($CaCO_3$) consisting of limestone is dissolved with rainwater containing carbon dioxide. The dissolution reaction is given as follows;

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^- \qquad (1)$$

Next the resulting acidic solution (pH equilibrated with 0.3 % CO_2 in air is 5.7) drops from the ceiling of caves, and then $CaCO_3$ precipitates as a result of volatilization of CO_2 and H_2O according to the inverse of Reaction (1). The column-like precipitate hanging from the ceiling is called stalactite, and the precipitate like a bamboo shoot on the floor is stalagmite. The growth rate of the city stalactites looks very fast, actually it was estimated to be ca. 7.5 mm/y, compared to well-known ca. 0.25 mm/y of natural stalactite. Such a fast growth of the city stalactites, in other words, fast dissolution of constituents of concrete bridges, results in the formation of cracks or voids within the body of bridges and causes the mechanical weakening of bridges. Acidic rainwater becoming an environmental problem accelerates the dissolution and the growth of city stalactites. In the present study, city stalactites were collected and characterized in detail.

2. EXPERIMENTAL

After taking *in situ* photographs of the city stalactites found in cities, some of them were collected and characterized by optical microscopy, scanning electron microscopy (SEM), X-ray diffractometry (XRD), energy dispersive X-ray spectroscopy (EDX), thermogravimetric/ differential thermal analyses (TG-DTA), and Fourier transform infrared spectroscopy (FT-IR).

3. RESULTS AND DISCUSSION

3.1 Preliminary observation

Figure 1 shows city stalactites hanging from a concrete bridge (building A) and a penthouse (building B). Both buildings were built in 1970s. The hanging scene resembles just that of natural stalactites. Figure 2 shows photographs of city stalactites collected from the building A. The cross sections of the city stalactites were almost colorless, however in some cases contained rusty colored spots or annual ring-like layers as clearly observed in sample A3. The city stalactites had hollows like a straw. The hollow opened at the front of the rods, which differs from natural stalactites with conically closed fronts. The open front suggests that the stalactite-forming solution, i.e., CO_2-containing rainwater, streamed comparatively faster in the city stalactites than in natural stalactites. The growth rate of the city stalactites was estimated to be ca. 7.5mm/y which is very fast compared to ca. 0.25mm/y of natural stalactites. The difference in growth rate could be related to the difference in dissolved compounds in concrete and limestone. Concrete minerals are *ca.* 25 % $Ca(OH)_2$, *ca.* 60 % calcium silicates, and others. Although the following reactions forming $CaCO_3$ are clarified [1,2];

$$Ca(OH)_2+CO_2=CaCO_3+H_2O \qquad (2)$$
$$Ca_3SiO_5+3CO_2+nH_2O=3CaCO_3+SiO_2\cdot nH_2O \quad (3)$$
$$Ca_2SiO_4+2CO_2+nH_2O=2CaCO_3+SiO_2\cdot nH_2O \quad (4)$$
$$CaSiO_3+CO_2+nH_2O=CaCO_3+SiO_2\cdot nH_2O \qquad (5)$$

where these calcium silicates are actually present as compounds called "C-S-H gel", such a fast growth rate of city stalactites was considered to be due to the existence of higher soluble $Ca(OH)_2$ than $CaCO_3$ and in addition easy volatilization of CO_2 from HCO_3^--containing solution (ref. Reaction (1)) in flowing air.

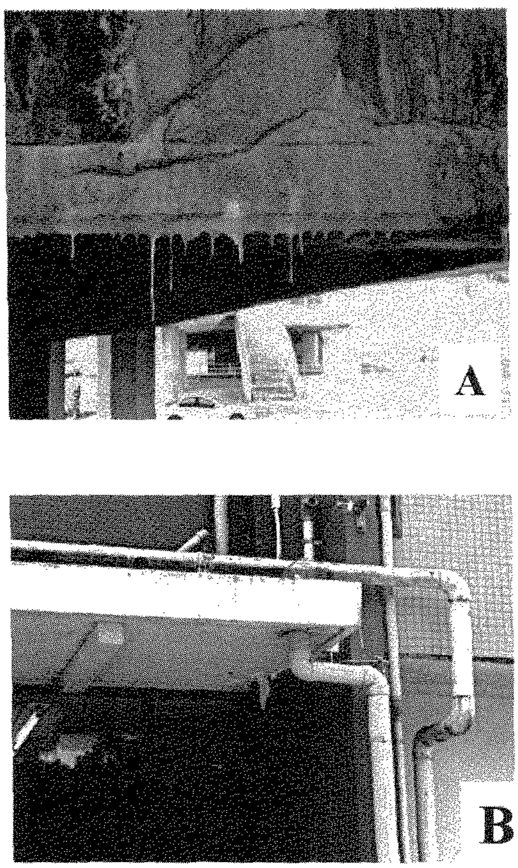

Fig.1 City stalactites hanging down from an old concrete bridge (building A) and a penthouse (building B).

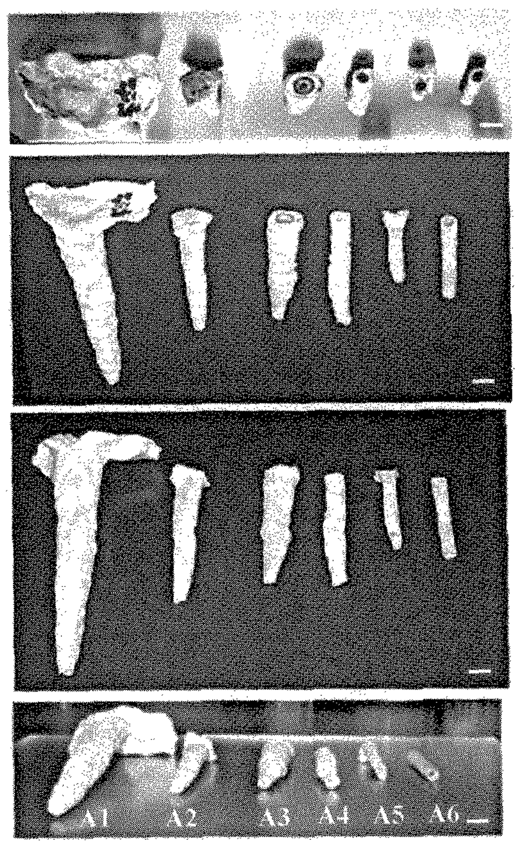

Fig.2 Photographs of city stalactites observed through different angles.
(Sample was collected from the building A)
Bar: 1 cm

3.2 Inside microstructure

Figure 3 shows optical and SEM photographs of sample A2. The cross section structure was constructed of annual ring-like layers with interlayer crevices, aggregated angular grains and a central hollow. Such a characteristic inside structure seemed to reflect the climate conditions during the stalactite formation. The inside wall of the hollow was constructed of transparent angular grains with 100 μ m in size. The crystal habit was characteristic of calcite-type $CaCO_3$ single crystals.

3.3 Impurity analysis

Figure 4 shows EDX spectra of sample A2. There were no elements other than Ca and O, which suggests pure $CaCO_3$ without impurities such as Fe, Si, S and others.

3.4 Mineral phase and its purity

Figures 5-7 show XRD patterns, FT-IR spectra and TG-DTA curves of sample A2 and reagent calcite-type $CaCO_3$. The stalactite and calcite showed almost the same patterns with each other.

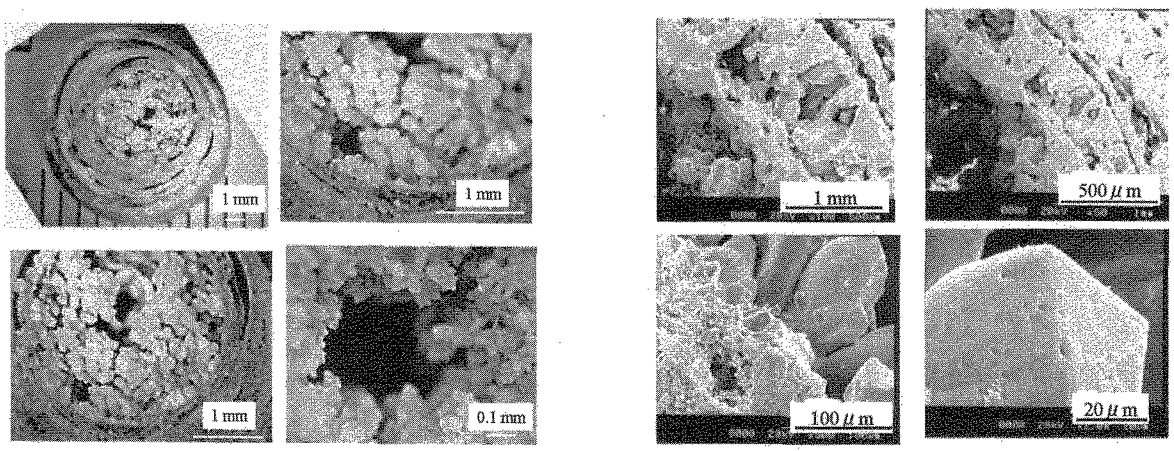

Fig. 3 Optical microscopic (left 4) and SEM (right 4) photographs of the cross section of city stalactite A2.

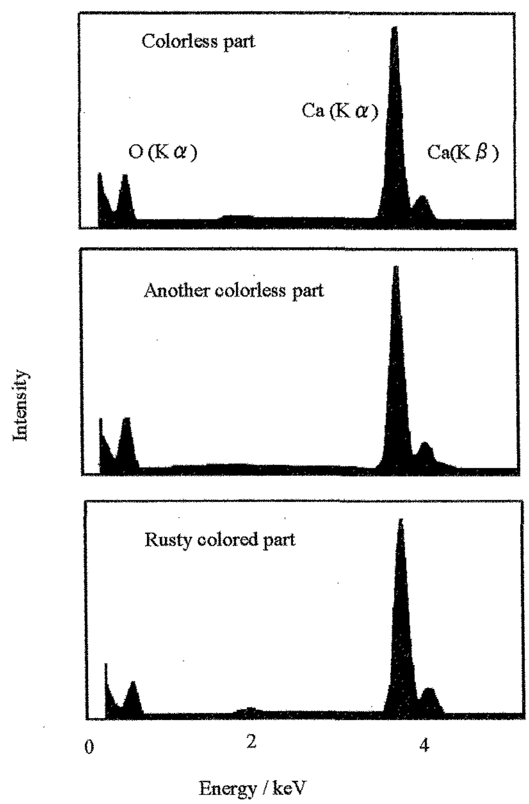

Fig. 4 EDX spectra of different parts of a cross section of sample A2.

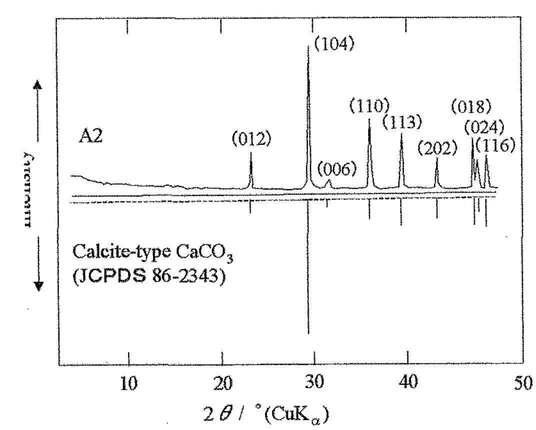

Fig. 5 XRD patterns of sample A2 and reagent calcite-type $CaCO_3$.

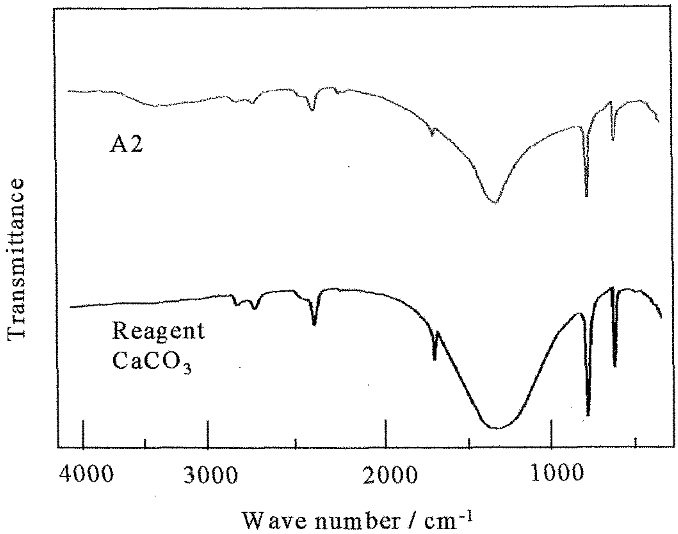

Fig. 6 FT-IR spectra of city stalactite A2 and reagent calcite-type $CaCO_3$.

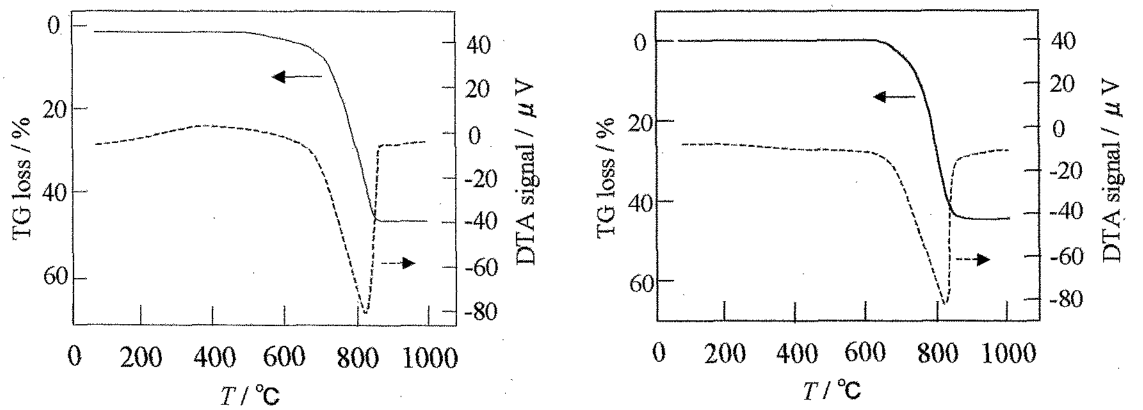

Fig. 7 TG-DTA curves of sample A2 (left, 57.1 mg) and reagent calcite-type CaCO3.(right, 36.5 mg). (10 / ℃, in quiescent air)

4. CONCLUSIONS

"City stalactites" collected from an old concrete bridge were characterized in detail. Every city stalactite had a straw-like hollow that was open at its front. A characteristic inside microstructure of the city stalactites seemed to reflect the climate conditions during the stalactite formation. The growth rate of the city stalactites was ca. 7.5mm/y. Such a fast growth rate compared to ca. 0.25 mm/y of natural stalactite could be related to a higher solubility of $Ca(OH)_2$ in concrete than that of $CaCO_3$ in natural stalactite. The mineral phase of the city stalactites was pure calcite-type $CaCO_3$. Impurities in the city stalactites were not detected.

References

[1] T.Yasue, *J. Soc. Inorg. Mater.*, **9**, 192-207 (2002).

[2] Y.Moriyoshi, Y.Chiba, M.Koiode *et al.*, *Phosphorus Res. Bull.*, **8**, 7-10(1998).

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