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### Study in salt weathering of reconstituted stones used in the Orval Abbey, Belgium

NGUYEN, Thi Hai Duong<sup>1\*</sup>, FUJIMAKI, Toshiaki<sup>2</sup>, OGUCHI, Chiaki T.<sup>3</sup>

<sup>1</sup>Dept. Civil & Env. Eng., Saitama Univ., <sup>2</sup>Graduate School of Sci. & Eng., Saitama Univ., <sup>3</sup>GRIS, Saitama Univ.

The Orval Abbey, a major monument of southern Wallonia, Belgium, was partly destroyed and rebuilt several times between the Middle Ages and the present time. The oldest parts are made of natural stones of Bajocian limestones (BJ) and Sinemurian limestones (SN), and the most recent parts are mostly made of reconstituted stones. The making process of reconstituted stones is not known. According to the previous studies, the reconstituted stones are much more susceptible to weathering than the natural limestones. To investigate the reason behind the salt susceptibility of the reconstituted stones, field works and laboratory investigations such as Mercury Intrusion Porosimetry, Scanning Electron Microscopy coupled with Electron Dispersive Spectroscopy, Ion Chromatography, X-Ray Diffractometry were carried out. Results of the estigations revealed that sulfur and sodium, which were the main source of the formation of the damaging sodium sulfate, have been detected in mortars, the soil water and river water, and the reconstituted stones themselves. Results of field works indicated that the temperature and humidity conditions of Site 3, where reconstituted stones were mainly used, fluctuated drastically compared with those of other sites. This condition favors the cyclic transformation of thenardite to mirabilite, which is known as the main damaging mechanism of sodium sulfate. Moreover, MIP analysis unveiled the fact that the pore size distribution of the reconstituted stones favored the salt damage, i.e. it consisted of large fraction of microporosity. The calculated salt susceptibility indices of reconstituted stones were also very high compared to those of natural limestones.

Keywords: weathering, sodium sulpfhate, thenardite, Oval Abbey, reconstituted stone

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## Influence of environmental conditions and test method on sodium sulfate weathering of four Japanese building stones

SWE, Yu<sup>1\*</sup>, OGUCHI, Chiaki T.<sup>1</sup>

<sup>1</sup>Geosphere Research Institute of Saitama University, <sup>2</sup>Geosphere Research Institute of Saitama University

Many standard and laboratory salt weathering tests have been elaborated to investigate the mechanisms of salt damage, which have threatened our priceless cultural heritage made of porous stones. The tests are also used to investigate the relative destructiveness of salts, and durability of different rocks for selecting proper ones for restoration works. Some results of these studies, however, have become debatable due to employing different test methods and environmental conditions. So far, comparative studies about test conditions are scarce. In addition, there are arguments about sodium sulfate, which is the most widely used salt in laboratory tests, as to which phase of the salt, i.e. thenardite or mirabilite, is responsible for the sodium sulfate damage. To solve these arguments, a series of laboratory experiments was performed by using two types of salt supply techniques: continuous partial immersion (CPI) and cyclic total immersion (CTI). Both tests were conducted under three different environmental conditions: (i) 20°C and 60% RH for 24 h (CPI 1); (ii) 45°C and 40% RH for 24 h (CPI 2); (iii) 45°C and 30% RH for 12 h and 10°C and 70% RH for 12 h (CPI 3); (iv) 3 h immersion at 20°C, 19 h drying at 45°C, and 2 h cooling at 20°C (CTI 1); (v) 3 h immersion and 21 h drying at 45°C (CTI 2); and (vi) 3 h immersion at 20°C, 17 h drying at 105°C, and 4 h cooling at 20°C. CPI 2 and CTI 2 tests were designed to investigate the destructiveness of sheer thenardite. All tests were run for fifty 24-h cycles. Prismatic specimens (5 x 5 x 15 cm3) of four types of Japanese building stones, namely Oya Tuff, Ashino Tuff, Indian Sandstone, and Tago Sandstone were used. A range of hydromechanical properties were investigated. For salt supply, saturated sodium sulfate solution (at 20°C) was used in all tests. It is observed that durability ranking of the rocks did not perfectly reflect their hydromechanical properties. Oya Tuff was consistently the least salt resistance in all of the tests, mirroring its properties. However, in contrary to their hydromechanical properties, Tago Sandstone, Ashino Tuff, and Indian Sandstone showed different durability against sodium sulfate in different tests, indicating the unreliability of rock properties in predicting salt susceptibility. Differing to what have been perceived, at the same upper-limit temperature, CPI tests were found generally more destructive than CTI tests, except for the extraordinarily aggressive CTI 3 test driven by a very high drying temperature. The results of CPI 2 and CTI 2 tests revealed that thenardite alone could cause significant damage, although the induced damage was smaller than that of mirabilite-involved tests such as CTI 1, CTI 3, and CPI 3. This suggests that in addition to the immense power of mirabilite attack, the contribution of thenardite in rock decay during drying cannot be discounted in CTI tests. In fact, it was the cyclic conversion of thenardite-mirabilite mechanism, which causes severe damage, no matter what salt supply technique is employed. Moreover, the two salt supply techniques produced markedly different damage patterns: CTI tests induced granular disintegration, spalling, fragmentation, or crumbling, whereas CPI tests mainly produced scaling, cracking, or efflorescing depending on environmental conditions and rock properties. The reason behind this is the continuous accumulation of salts deep inside the CPI-specimens, which produced severe internal cracking and thick scaling, in contrast to the cyclic disintegration of outermost surfaces of CTI-specimens, which did not favor the salt accumulation.

Keywords: salt weathering, continuous partial immersion, cyclic total immersion, thenardite, mirabilite

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#### Mineralogical characterization of a stone by using colorimetry

NAKAYAMA, Taishi<sup>1\*</sup>, OGUCHI, Chiaki T.<sup>2</sup>

<sup>1</sup>GRIS, <sup>2</sup>GRIS,Saitama Univ.

In this study, the possibility of the exploitation of visible-reflectance spectrum as the technique to non-destructively specify the mineral species in situ was investigated. Color measurement of various samples was performed using colorimetry. Samples employed were reagents and standard samples, such as a argillite i.e., quartz, common feldspar, sodium feldspar, white mica, calcite, hematite, magnetite, limonite, a sulfide of iron, calcium sulfate, kaolinite, bauxite, calcium carbonate, sodium sulfate, red iron ore, limonite, aluminum sulfate, sodium chloride, sodium hydrogen sulfate, and potassium alum. In addition, salts and moss adhesive rock samples extracted from the Orval Abbey of Belgium, and salts collected from the Yoshimi-hyakuana were also measured. In order to examine the possibility of mineral specification by a color spectrum, it is necessary to (1) measure the color of a standard sample, (2) measure the color of the mineral extracted from the field, and (3) identify the mineral by more laboratory-based techniques, such as SEM-EDS and XRD. After the examination, it turned out that the spectrum of the sample extracted from the fields and the spectrum of a corresponding standard sample looked very similar. It is also observed that the color spectrum could better describe a very small quantity difference, rather than the L\*a\*b\* value. It is concluded that the identification or specification of a mineral using the visible-reflectance spectrum technique is possible. However, there still are many difficulties, such as construction of a database and examination of an error of measurement, to address in order to successfully employ this technique in field.

Keywords: mineral species, visible-reflectance spectrum, color measurement

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#### Dissolution rate of limestone at a doline in the Akiyoshidai karst plateau

Sanae Akiyama<sup>2</sup>, HATTANJI, Tsuyoshi<sup>1\*</sup>, MATSUSHI, Yuki<sup>3</sup>, Yukinori Matsukura<sup>4</sup>

<sup>1</sup>Faculty of Life and Environmental Sciences, University of Tsukuba, <sup>2</sup>Graduate School of Life and Environmental Sciences, University of Tsukuba, <sup>3</sup>Disaster Prevention Research Institute, Kyoto University, <sup>4</sup>University of Tsukuba

The spatial variation of limestone dissolution rates is significant for landform evolution of karst terrain including doline. Although many laboratory experiments and field observations have elucidated dissolution rate of limestone under specific conditions, but few studies estimated dissolution rates in situ around doline. This study aims to estimate the current rate of dissolution at a doline in the Akiyoshidai karst plateau in Yamaguchi Prefecture, combining the following two methods. One is electric resistivity survey and measurement of soil property, which reveal subsurface structure of the doline including the depth of the soil-rock interface and the spatial variations of soil moisture contents. The other is weathering experiments and hydrological observations, which reveal the relationship between limestone dissolution rates and the environmental factors including moisture contents, water chemistry, temperature, and  $CO_2$  concentration.

Electrical resistivity imaging (ERI) survey reveals spatial variations of resistivity in soil or bedrock below slope and bottom of the doline. Comparing the result of the resistivity imaging with manual sounding using a cone penetrometer, resistivity value of 300 ohm m approximately corresponded to the soil-rock interface ranging from 1 m deep at upper doline slope to 10 m deep at bottom of doline. Low resistivity (50-100 ohm m) zones, which are equivalent to saturation zones, existed above the soil-rock interface even in drier seasons, indicating that soil is hydrologically saturated through the year immediately above the soil-rock interface.

In the field weathering experiment, limestone tablets (rock fragment of 3.5 cm in diameter and 1 cm thick) were buried in soil at 4 sites of the doline: S1 located at the upper slope; S3 located at the middle of slope; S5 located at the lower slope; S6 located at bottom of the doline. In these sites, soil moisture contents and ground temperature were monitored 10-min intervals, and manual measurement of concentration of  $CO_2$  in the soil air and soil water sampling were carried out about every two months. The experiments and observation were conducted for total 768 days from 2009 to 2011.

The dissolution rates of tablet were 1.6-3.3%/y at S1 and S3, where soil moisture saturation sustained for a long time after precipitation. The smallest dissolution rate was 0.11-0.55%/y at S5, where the period of high soil moisture was short after precipitation. The result of regression analysis revealed that dissolution rate of tablets were strongly controlled by  $W_{97}$  (R<sup>2</sup>=0.65), which is defined as the proportion of the duration of saturation (degree of saturation >97%) to whole time of the experiment . Furthermore, combination of two variables,  $W_{97}$  and mean value of estimated CO<sub>2</sub> concentration show a stronger correlation with dissolution rate of tablets (R<sup>2</sup>=0.74), although  $W_{97}$  primary controls dissolution rate of limestone tablets.

For the case that the soil immediately above the soil-rock interface is saturated ( $W_{97}$  of 100%) throughout year, dissolution rate of limestone would be 3.90%/y, which corresponds to denudation rate of 137 mm/kyr. This rate is slightly faster than the long-term denudation rates inferred from cosmogenic <sup>36</sup>Cl concentrations at the same site. Low resistivity zones with high soil moisture also exist beneath some parts of the slope as well as the bottom of the doline, implying that such slopes have a fast dissolution rate equivalent to the bottom of doline.

Keywords: limestone, karst, doline, electric resistivity survey, dissolution rate

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# Granulomeric and mineralogic investigation of liquefaction induced by the 2011 megaquake at the Watarase flood-retarding

SETO, Masayuki<sup>1\*</sup>, Takaaki Asai<sup>2</sup>, Toshiyuki Kitazawa<sup>2</sup>, OGUCHI, Chiaki T.<sup>1</sup>, TAMURA, Toshikazu<sup>2</sup>

<sup>1</sup>Geosphere Research Institute of Saitama University, <sup>2</sup>Rissho University

The 2011 Off Pacific Coast of Tohoku earthquake of Mw9, which recorded a seismic intensity of JMA scale 6 in central Kanto, induced liquefaction at the northwestern part of the Watarase flood-retarding basin in the central part of the Kanto basin. The area is located in a former pond into which floodwater of the Watarase river and a few tributaries flew frequently. We collected boiled sand and carried out boring investigation to loosely-deposited sand and mud alternation at four sites (sites A-D) to identify the layers which caused liquefaction. At site D, we had a 500cm deep core sample. We observed some layers; 0-30cm: artificial ground, 30-70cm: silt, 70-250cm: medium or fine sand, 250-400cm: clay, 400-500cm: medium sand. Ground water level was 200cm deep. Bowling sites A, B and C were almost similar to site D. Grading and mineral analyses carried out by liquefaction layer was the medium and fine sand of around 200cm deep. In comparison of granulometry and mineral composition of boiled sand with those of borehole-core samples below watertable, we identified the layers which were liquefied as follows: site A- medium and fine sand (134-157cm deep) and medium sand (187-232cm deep), site B-coarse or medium sand (160-195cm deep), site C-fine sand (193-255cm deep), site D-fine sand (210-245cm deep) and fine sand (399-422cm deep). All the liquefied sandy layers are correlated to the uppermost members of the Holocene deposits which were interpreted to have been formed during recent 2000years.

Keywords: The 2011 Off Pacific Coast of Tohoku earthquake, liquefaction, grading analysis, mineral analysis, central part of the Kanto basin, Watarase flood-retarding basin