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Salt Weathering on Buildings and Stone Sculptures

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Salt weathering susceptibility of natural limestone and reconstituted stone used in the Orval Abbey, Belgium.

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ABSTACT

To understand the weathering of the building stones observed at the Orval Abbey (Belgium), rock properties were investigated and a series of experiments were performed. The older buildings of the abbey were constructed using Bajocian and Sinemurian limestones. The materials employed in the newer buildings ironically deteriorate at the abbey site; these are mostly reconstituted stones made by agglutinating crushed pieces of aforementioned limestones with cement. Salt weathering experiments were carried out not only on the three Orval stones but also on Savonniére limestone (France) and Oya tuff (Japan). Experiment A, a capillary test using Na_2SO_4 solution at constant temperature of 20°C, showed that the reconstituted stone had the fastest rates of capillary rise and were completely destroyed. In experiment B, which was performed at fluctuating temperatures of 10-30°C, the reconstituted stone and Oya tuff were destroyed. Considering volume fraction of pores of different sizes such as 10, 1, 0.1 and 0.01 μm, it is concluded that debris production and hardness reduction are influenced by 0.01 μm and 10 μm pores, respectively.

Keywords: Orval Abbey, Salt weathering, Debris production, Equotip hardness, Reconstituted stone

1 INTRODUCTION

The Orval Abbey, a major monument in Wallonia, Belgium, has a long and polyphasic history (Thomachot-Schneider et al., 2010). The first Abbey was built more than 1000 years ago, but was destroyed in 1637 during the French-Spanish war. The mediaeval abbey was subsequently restored, however, the site was destroyed again by the French insurgents in 1794 during the French Revolution. A new abbey was built by the Cistercian commandment in the beginning of 20th century. However, the new building is suffering from damages mainly by salt weathering. Thomachot-Schneider et al. (2010) reported that the stones used in the new abbey are artificially made using limestone fragments agglutinated with cements. The present paper investigates the characteristics of the artificial rock using experimental approaches.

2 BUILDING STONES USED IN THE ORVAL ABBEY

Three types of stones are used in the Orval Abbey (Figure 1). According to Thomachot-Schneider et al. (2010), they are the original Sinemurian limestone, the original Bajocian limestone and blocks of reconstituted stones. The Sinemurian limestone is a homogeneous sandy limestone constituting the geological substratum in Orval (Luxemboug formation). The limestone from local quarries is used in the building foundation. The Bajocian limestone belongs to the Longwy formation and contains organic remains. This limestone is significantly porous and for this reason it is mainly used for the main building

(Figure 1a). Most of the Bajocian limestone used in the Orval Abbey was taken from the Pas-Bayard quarry, which is already abandoned, located about 30 kilometers southeast of the Oval area.

The reconstituted stones are mainly used in the Modern Abbey (Figure 1b). During its construction, in order to save natural limestone resources and to reduce costs, debris removed from the ruins and wastes of natural freestone cutting were agglutinated using cements. This stone was produced from 1932 to the completion of the Modern Abbey in 1948, however, the information about the making process and the composition are hardly known. The only certain information is that different craftsmen at the site of the abbey made the reconstituted stones using rock debris found in the ruins of the old Abbey and fragments produced by cutting the Bajocian limestone blocks (Thomachot-Schneider et al. 2010).

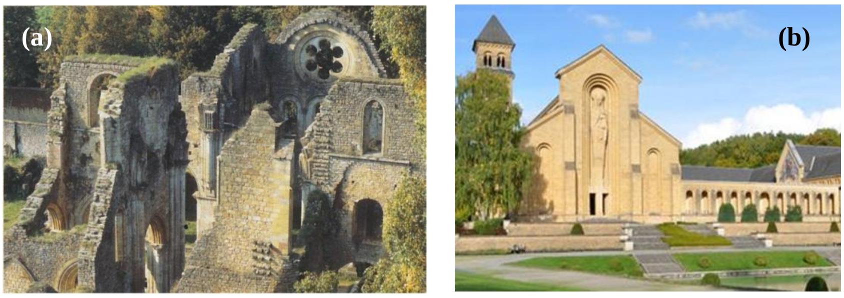

Figure 1. Overview of the Orval Abbey. (a) Ruins of the mediaeval abbey. (b) The modern abbey.

3 EXPERIMENTAL DESIGN

3.1 Materials

Five kinds of building stones were used in the series of experiments of the present study. Three of them, namely Sinemurian limestone (SN), Bajocian limestone (BJ) and reconstituted stones (RS), were collected from the Orval Abbey. The other two are the *Savonniére* limestone (SV) from north France and Oya tuff (OY) from central Japan, which are commonly used as building stones in their respective areas. *Savonniére* limestone was used for restoration works in *Cathedral du Reims* in France at the beginning of 20th century (Figure 2a). It has a slightly pink colour, which is the reason why it is suitable for use in the restoration of the cathedral. It is also said that the *Savonniére* limestone has larger pores than the original building stone (Couvielle limestone) of the cathedral (Moreau et al., 2008; Osawa, 2009). The imported *Savonniére* limestone available in Japan was used for the experiments of the present study.

Oya tuff is categorized as a green tuff in Japan. It was originally deposited as a rhyolitic ash in the old Sea of Japan during the Miocene (Nakamura et al. 1981; Oguchi & Yuasa, 2010). The rock has the advantages of being easily cut and processed, which is why it has been used for buildings such as the Tokyo Imperial Hotel and the Matsugamine Catholic Church (Figure 2b). The tuff block cut from one of the underground quarries was used in the experiments. The five stones were cut into cylindrical specimens measuring 4.5 cm in diameter and 5 cm in height (Figure 3). The cut surface was ground using #800 carborundum.

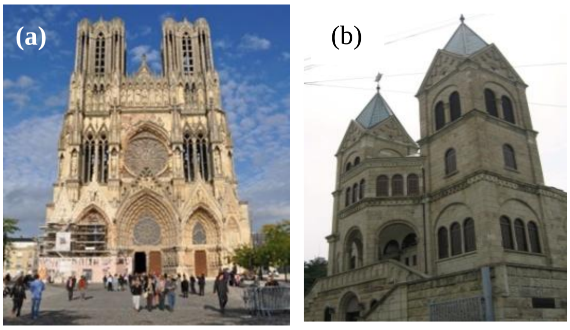

Figure 2. Overview of buildings made by stones used in the present experiments. (a) Cathedral du Reims in France. (b) Matsugamine Church in central Japan.

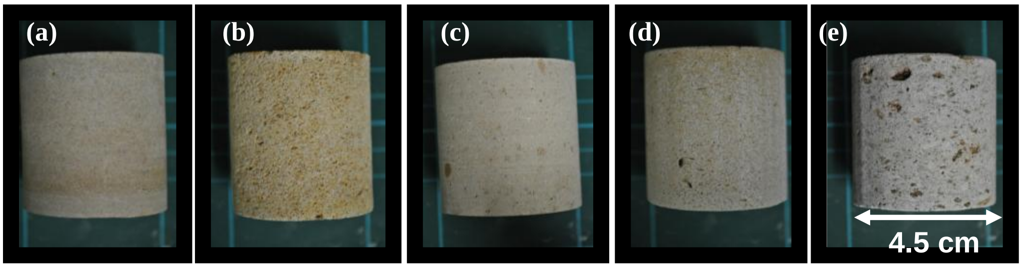

Figure 3. Rock specimens used in the experiment. (a) Sinemurian limestone (SN). (b) Bajocian limestone (BJ). (c) Reconstituted stone (RS). (d) *Savonniére* limestone (SV). (e) Oya tuff (OY).

3.2 *Rock properties*

Rock properties, such as true density, bulk density, porosity, tensile strength and surface hardness of the three stones were investigated. Bulk density (ρ_{bulk}) was calculated by dividing the dry weight (W_d) by the volume (V) of specimens after 24 hours drying at 110°C in an oven. The values of true density, ρ_{true}, were obtained according to JIS A 1202. The porosity (n) was calculated from the equation, $(\rho_{true}-\rho_{bulk})/\rho_{bulk}$. Pore size distributions of the connected pore volume (V_{total}) for pore diameter ranging from 0.003 to 200 μm were measured using Autopore IV mercury intrusion porosimeter (Micromeritics®). Tensile strength (S_t) was tested under dry conditions. Equotip hardness test was also performed in order to evaluate the hardness reduction during the experiment. Equotip index (L) of hardness values is represented by the values obtained by dividing repulsion speed by initial speed and multiplied by 1000. The average values of 20 hits at each point in the middle of specimens were adopted.

Table 1. Physical and mechanical properties of the five rock type

Samples	True density (g/cm^3)	Bulk density (g/cm^3)	Porosity (%)	Tensile strength (MPa)	Equotip hardness (L)
SN	2.74	2.39	12.94	4.82	679
BJ	2.74	1.79	34.79	1.38	362
RS	2.67	1.90	29.00	3.05	588
SV	2.71	1.63	39.79	1.41	415
OY	2.36	1.44	38.69	1.85	606

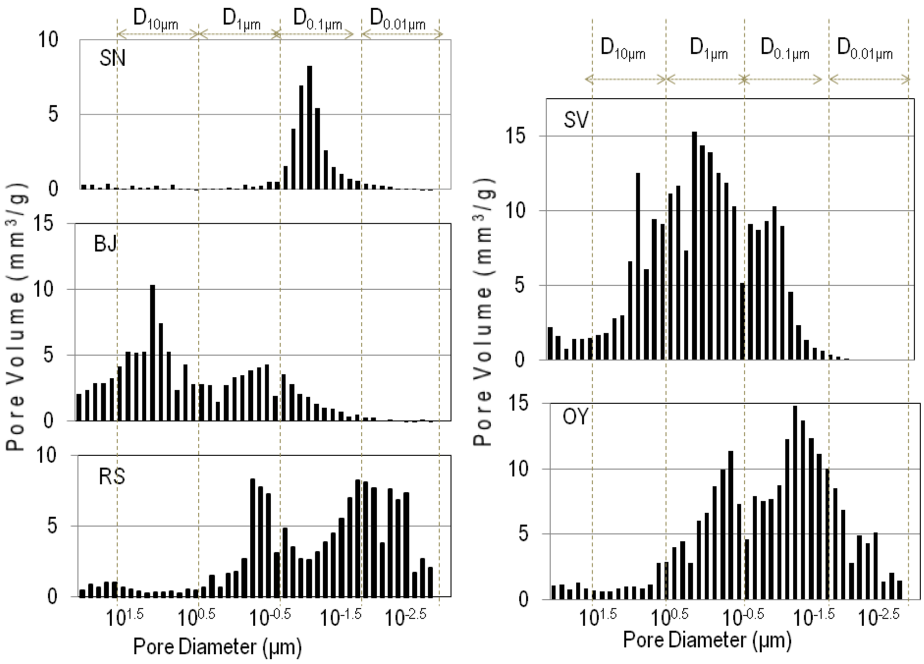

Figure 4. Pore size distribution of the five rocks measured by mercury porosimetry.

Table 1 shows the results of rock characterization tests. Limestones have relatively higher true density, whereas Oya tuff has lower true density because of glassy rhyolitic components. Sinemurian limestone (SN) has higher bulk density, tensile strength and Equotip hardness and lower porosity than other rock samples. Bajocian limestone (BJ), Savonniére limestone (SV) and Oya tuff (OY) have similar values of bulk density, porosity and tensile strength. However, the Equotip hardness of OY is much higher than other two limestones because of its sensitiveness to the surface roughness of rocks. The reconstituted stone (RS) shows the intermediate properties between SN and BJ.

Results of pore size measurement are shown in Figure 4. For clear expression, pore sizes are defined based on pore diameter; i.e., $D_{10\mu m}$, $D_{1\mu m}$, $D_{0.1\mu m}$ and $D_{0.01\mu m}$, representing the poreswith diameters between $10^{1.5}$-$10^{0.5}$µm, $10^{0.5}$-$10^{-0.5}$µm, $10^{-0.5}$-$10^{-1.5}$µm and $10^{-1.5}$-$10^{-2.5}$µm, respectively. The dominant pore size for SN, which has a low porosity, is $D_{0.1\mu m}$. Hence, SN may be characterized as a dense rock with small pores. On the contrary, BJ has a large amount of $D_{10\mu m}$ pores. RS is characterized by small pores with $D_{0.01\mu m}$. SV has many pores with diameters $D_{10\mu m}$, $D_{1\mu m}$ and $D_{0.1\mu m}$. OY is characterized by a large amount of pore volumes of $D_{1\mu m}$ and $D_{0.1\mu m}$.

3.3 Experimental methodology

Cylindrical specimens of SN, BJ, RS, SV and OY with similar rock properties were used in *Experiment A*. The experiment was performed at 20°C using saturated Na_2SO_4 solution (16%), half concentration of the same solution (8%) and distilled water as a control (Figure 5). In this experiment, the bottom of the oven-dried specimens was partially immersed into the solutions up to the height of 0.5 cm to ensure continuous supply of salt solution. For a period of 24 hours from the start of the experiment, observations and weight measurements were made at designated intervals of time. Thereafter, the weights of specimens which now contained the absorbed solution as well as crystallized salt, were measured and the solutions were replenished every 12h.

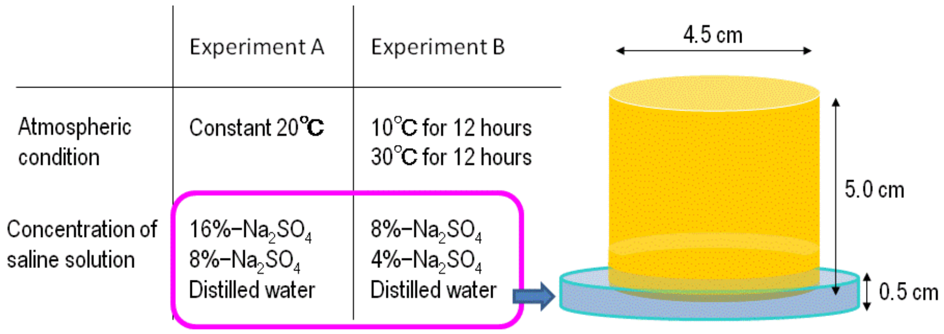

Figure 5. Outline of experimental method.

Experiment B was performed at 10-30°C using 8%− and 4%−Na_2SO_4 solutions and distilled water. The reason why the different concentrations were adopted between Experiments A and B is that the solubility of Na_2SO_4 at 10°C is much lower than that at 20°C. The bottoms of the oven-dried specimens were similarly immersed into the solutions up to the height of 0.5 cm. Two temperature regimes (10°C for 12h and 30°C for 12h) were set in an incubator (Takeda Rika Co. Ltd.: FMU-133I) (Figure 5).

At the end of both experiments, the salts accumulated inside and on the specimens were rinsed with distilled water. Observations and weight measurements were made frequently during the first 24h. Then, measurements of total weights and replenishment of solutions were done every 24-hour. Eighteen cycles were repeated throughout the experiment. After both experiments the salt accumulation on the specimen was rinsed using distilled water. As debris produced by salt crystallization during the experiments was initially agglutinated by salts, much more debris was released after leaching the salts. The detached debris was then sieved using the 4.75 mm and 1.18 mm mesh. The residual materials in the sieve were dried and weighed. The hardness of the remnants of the specimens, except for the ones completely destroyed, was investigated using Equotip hardness tester.

4. RESULTS OF THE EXPERIMENTS

The RS specimen showed the fastest rates of capillary rise with 16%-Na_2SO_4 solution. Salts crystallized on the surface of the RS specimen within 1 h from the beginning of Experiment A. Efflorescence was observed on the specimen immersed in 8%-Na_2SO_4 solution after 5 hours had passed from the beginning of Experiment A. At the end of the capillary rise test, RS was completely destroyed but other specimens were not, although BJ and SV were slightly deteriorated on their tops (Figure 6).

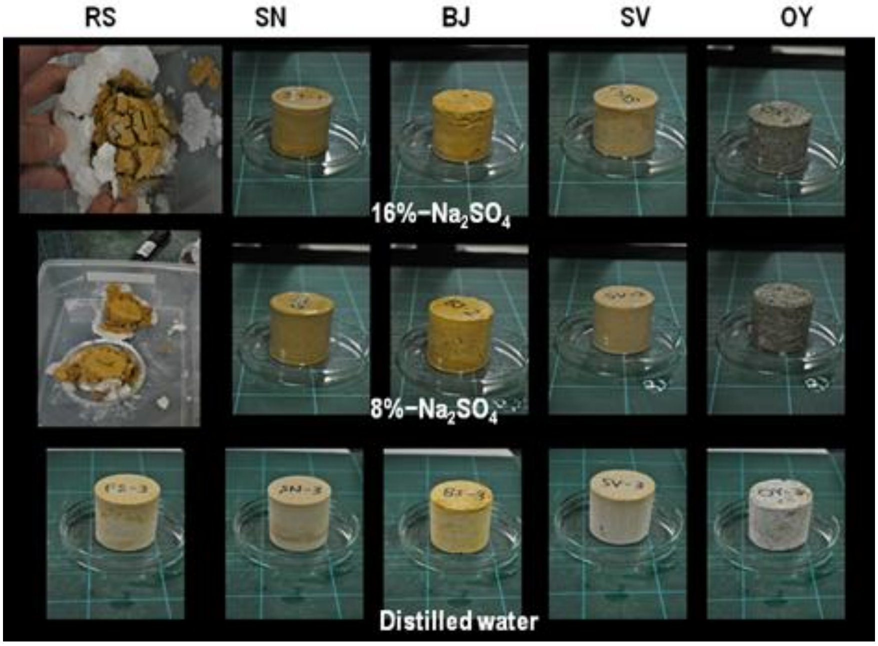

Figure 6. Observation of specimens after Experiment A.

On the other hand, the specimens used in Experiment B were damaged even though the solution concentration was lower. The RS and OY specimens treated with 8%-solution in Experiment B suffered more damage than those treated with 8%-solution in Experiment A. The 4%-solution treated RS and OY specimens of Experiment B were also destroyed, although they suffered less damage than those treated with 8%-solution in Experiment B. The 8%-solutions attacked the RS and OY specimens from inside and destroyed them completely, whereas the 4%-solution only induced crack propagation (RS) or produced powdery flaking on the surface of the specimen (OY). It is observed that RS has lower durability against salt weathering, although it has higher strength than BJ and SN. Figure 7 shows the debris production ratio (R_{debris}) calculated by dividing debris weight with initial specimen weight. The RS and OY specimen produced substantial amount of debris during the experiments. Other specimens were not destroyed significantly. The reason why OY of Experiment B produced much debris is considered to be explained as follows. OY itself is tend to be damaged by wet/dry weathering because it contains small amount of expansive clay minerals such as smectite and has many micro pores. Although it is not clearly explained, RS might have concentration reliance against wet/dry weathering due to Na_2SO_4.

Figure 8 shows the results of Equotip hardness test before and after the experiments. The values show averages of 20 times hitting of each specimen side. Even for the extremely low-weathered specimens, i.e., less debris production such as SN, BJ and SV, hardness values declined after the experiments. Although the reason is not clearly explained, insignificant damages might be occurred on these specimens.

5. DISCUSSION

The results of Experiments A and B were evaluated by (1) debris production for highly damaged specimens; and (2) Equotip hardness values for the specimens showing lower degree of weathering.

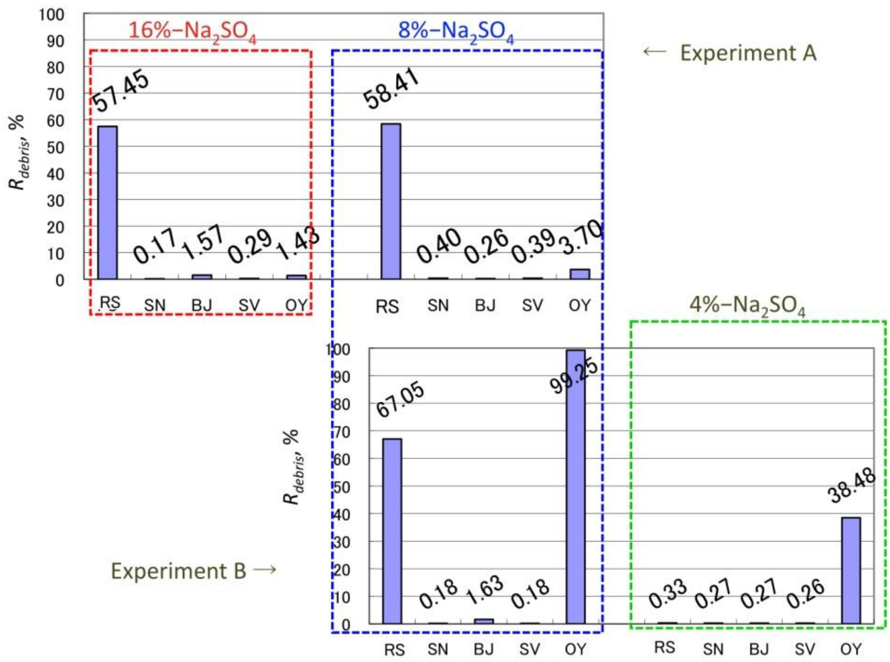

Figure 7. Debris production rates after the experiments.

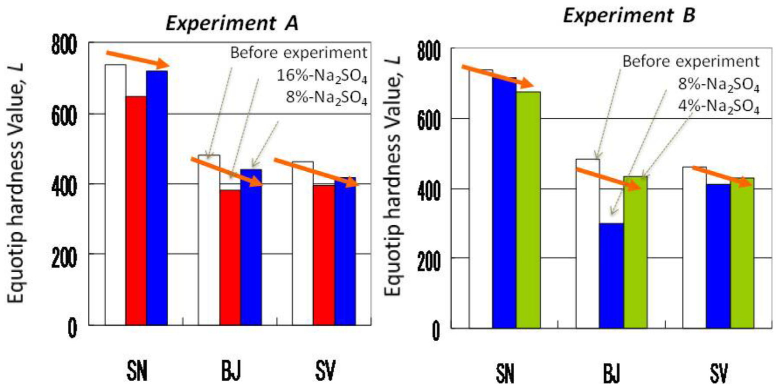

Figure 8. Result of Equotip hardness test.

The highly deteriorated specimens, RS and OY, actually have a large amount of pores ranging from 0.01μm to 1μm in diameter. The importance of micropores in crystallization damage has often been pointed out in the literature (e.g., Swe Yu & Oguchi, 2010). Therefore, the relationships between debris production ratio (R_{Debris}) and the volume fraction of pores with certain diameter ranges ($R_{pore\text{-}\mu m}$) were examined (Figure 9). It is shown that the R_{Debris}-values increase with increasing volume fraction of pores with a diameter of 0.01μm, although the results of Experiment A using 16%-Na_2SO_4 solution are obscure. However, little significant relationships between the R_{Debris}-values and pores with diameter ranges of 0.1, 1 and 10μm were indicated. Although it is not clearly explained the reason from these limited experimental data, it is considered that smaller pores were more affected than lager pores because salt crystallizes from micropores first and then middle- to micro-pores. In order to clarify this, it will be necessary to investigate from not only pore properties but also wide aspects including intensive mineralogical investigations.

The relationship between the reduction ratio of Equotip hardness (R_{Equo}) and the volume fraction of pores with a certain diameter range ($R_{pore\text{-}\mu m}$) were also examined (Figure 10). It shows that the R_{Equo}- values increase with increasing volume fraction of pores with a diameter of 10μm. However, little significant correlations with other pore ranges were indicated. The possible reason is considered as follows, although limited data were obtained from these experiments. Equotip

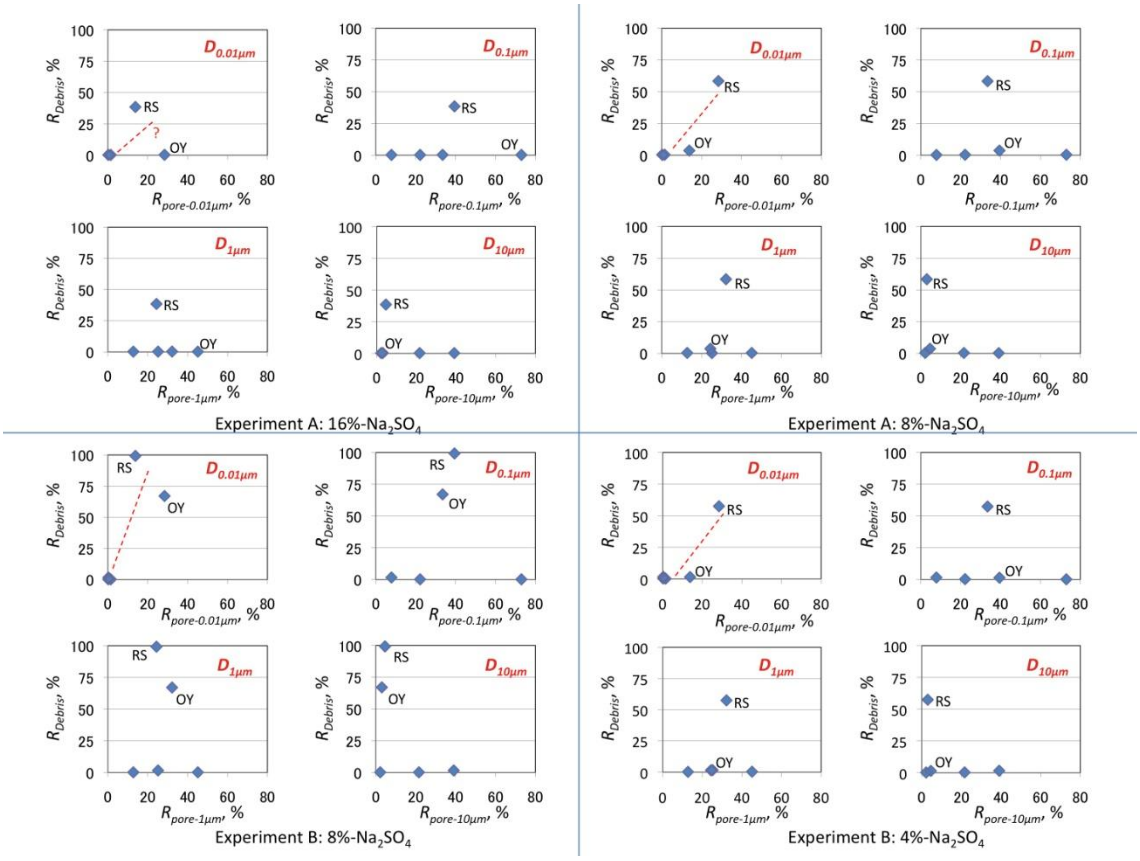

Figure 9. Relationship between volume fraction of pores ($R_{pore\text{-}\mu m}$) and debris production ratio (R_{Debris}).

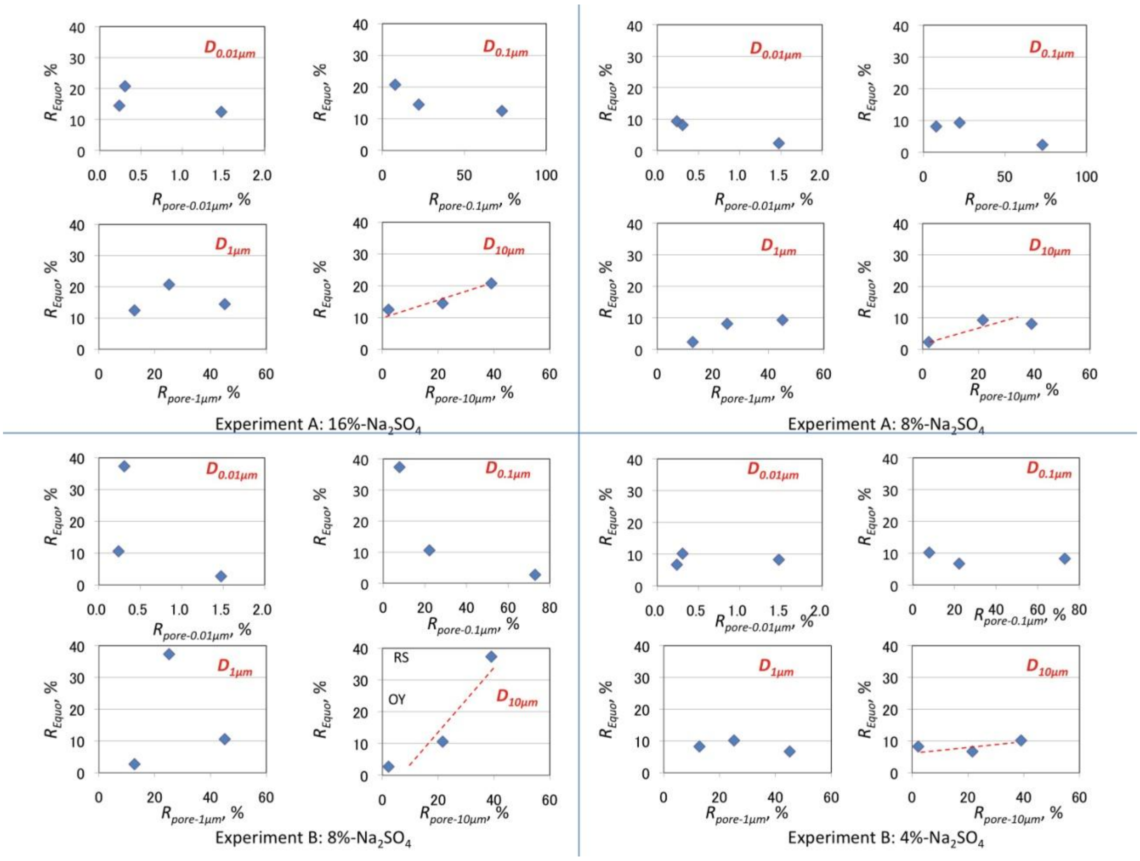

Figure 10. Relationship between volume fraction of pores ($R_{pore\text{-}\mu m}$) and hardness reduction ratio (R_{Equo}).

hardness was measured using massive specimens survived from the experiments after rinsed salts off, whereas the most salt-affected part was used for debris production measurement. This means that the Equotip test tends not to evaluate the part including many smaller pores affected by salt crystallization. In addition, Equotip values decrease with increasing diameters of micro-pits on the weathered surface (Aoki et al., 2010), which suggests that the values are affected by lager pores.

Consecutive processes were, therefore, considered as follows; i) salts crystallize first from micropores and then micropores are damaged, ii) fine debris were produced, so that the relationships between R_{Debris} values and $R_{pore\text{-}1\mu m}$ were recognized, iii) pores enlarged in the remained massive part, iv) Equotip hardness obtained from the survived massive part were decreased. The reason for deterioration due to salt weathering observed at the new Orval Abbey building can be elucidated by higher volume fraction of micropores with a diameter of 0.01μm in reconstituted stone (RS), although more results will be necessary for more convictional explanation

6. CONCLUSIONS

To measure the salt susceptibility of building stones used in the Orval Abbey, Belgium, rock property analysis and salt weathering experiments were performed using two natural limestones and a reconstituted stone from the Abbey and the results were compared with stones commonly used in France and Japan. Throughout the series of experiments, the reconstituted stone was completely destroyed during the partial immersion test using Na_2SO_4 solution at a constant room temperature of 20°C. The reconstituted stone and Oya tuff used in the experiment at a fluctuating temperate of 10-30°C were also destroyed. The debris production ratio and the hardness reduction ratio are correlated with the volume fraction of pores with diameters of 0.01μm and 10μm, respectively. The debris production ratio is useful for evaluating weathering products, whereas the Equotip hardness test has an advantage in evaluating residual rocks.

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