Formation Mechanisms of Beachrocks in Okinawa and Ishikawa, Japan, with a Focus on Cements*1

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Beachrock is a type of sedimentary deposit held together mainly by calcium carbonate cement in the tidal zone of sandy beaches in tropical and subtropical regions. Man-made beachrock has the potential to inhibit coastal erosion; considering this important application, we performed field investigations and laboratory tests to understand the formation mechanisms of beachrocks in Okinawa and Ishikawa, Japan. We performed a needle penetration test, microbial population count and urease activity test, and conducted elemental and mineral analyses. Our investigation showed that in Okinawa the evaporation of seawater and/or urease activity of the microorganisms may have resulted in precipitation of high Mg calcite, leading to the formation of beachrock. In Ishikawa, beachrock and sand were present near a spring with a relatively high concentration of Al3+. The mixing of spring water (pH 4.7) with seawater could have led to the precipitation of the Al- and Si-bearing cement that is consolidating the sand particles, leading to development of beachrock. [doi:10.2320/matertrans.M-M2013844]

(Received October 11, 2013; Accepted December 13, 2013; Published February 7, 2014)

Keywords: beachrock, formation mechanism, cement, unconfined compressive strength

1. Introduction

Coastal erosion is a significant problem along the world’s coasts. To preserve coastlines, various methods are used. These include construction of artificial reefs and headlands, detached breakwaters and hard shore protection, which control the amount of drift sand and/or beach nourishment and sand bypassing, and thus overcome the shortage of drift sand. However, these solutions are expensive, and require long time periods and the engineering of large amounts of materials, especially for heavyweight sand coasts.1,2)

As an alternative countermeasure against erosion, we consider here the use of man-made rocks that auto-repair by means of sunlight, seawater, and bacteria. Our model of artificial rock is beachrock. Beachrock is a type of sedimentary deposit that generally occurs on tropical and subtropical beaches as a result of intertidal lithification of loose beach sands and gravels by carbonate cementation.3) Beachrocks around the world have been reported to form over several thousand years e.g.,4,5) owing to interactions among sand supply, cement precipitation from seawater and coastal erosion by ocean waves. Therefore, it may be possible to slow the erosion of coasts by making man-made beachrock from coastal sands. Because this artificial rock is made of local materials (i.e., seawater, sand, bacteria), it has the potential to be an eco-friendly product.

In this study, we performed field investigations and laboratory tests to understand the formation mechanisms of beachrocks in Okinawa and Ishikawa, Japan, because understanding this mechanism is an important step in making artificial beachrock. As part of this analysis, we performed a needle penetration test, determined the viable bacterial count, performed elemental and mineral analyses of the beachrocks and sands, and analyzed both seawater and spring water near the studied beachrock sites. Our focus is on the cement formation mechanism of beachrock, which occurs in the intertidal zone. Cement type and content have the potential to influence the strength of the material; hence, detailed knowledge of beachrock cements is valuable for producing a man-made equivalent.

2. Study Sites

2.1 Sumuide, Nago, Okinawa, Japan

The geology of Sumuide, Nago, Okinawa, Japan (site O; Fig. 1) comprises limestone and calcarenite of the Quaternary Ryukyu Group.6) The location is 26° 40′ 74″ N and from 126° 00′ 73″ to 126° 00′ 74″ E.

2.2 Shibuta, Wajima, Ishikawa, Japan

The second site is Mitsuko beach in Shibuta, Wajima, Ishikawa, Japan (site I; Fig. 1, 37° 26′ 20″ N and 137° 02′ 17″ E). This site consists of Neogene Akagami mudstone strata,7) which contain diatoms.

3. Methods

3.1 Needle penetration test

At each site, needle penetration grade (Np) values of some beachrock samples (i.e., exposed beachrock near the seawater and buried beachrock under the coastal sand) were measured by a needle penetration device (SH-70, Maruto Testing Machine Company, Tokyo, Japan). Unconfined compressive strength, quo, was estimated from Np by the correlation chart of Np and from quo described in the instruction manual.

3.2 Microbial population count

Seawater, some beachrock samples, and sand at both sites were collected in sterile test tubes and refrigerated at 4°C in our laboratory. Subsequently, 1.0 g of each sample was mixed with 9 mL of artificial seawater (Akuamarine, Yashima Drug Company, Osaka, Japan) or saline solution (1.0 g/L poly-peptone and 8.5 g/L NaCl with distilled water), and 10 µL of the supernatant was added to ZoBell2216E medium

*1This Paper was Originally Published in Japanese in J. MMIJ 129 (2013) 520–528.
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(for marine bacteria) or polypeptone-yeast extract medium\(^8\) (for viable bacteria). About marine bacteria, ZoBell2216E medium is used to obtain the standard colony counts.\(^9\) After inoculation, the media were incubated at 25°C for 7 days. Subsequently, each population (colony count) was counted by the plating method. Because the populations increased with time and were stable around 7 days later, we set the curing period at 7 days.

3.3 Urease activity test

We isolated colonies from the sand adjacent to beachrock at site O using ZoBell2216E medium. Each colony was mixed with 20 mL of solution (25 g/L CO(NH\(_2\))\(_2\) and 20 mL/L cresol red solution with distilled water) in a 20 mL bottle. Under sealed conditions, the samples were left standing at 45°C for 2 h. To determine whether the colonies have urease activity, we observed the solution color after 2 h. For cresol red, a change from yellow to purple can be observed from pH 7.2 to pH 8.8.\(^10\) Those samples that changed to purple were measured for their pH values. For comparison, a non-bacterial sample was measured as well.

3.4 Elemental analyses and SEM observation

Samples of exposed beachrock, buried beachrock, and adjacent sand were analyzed by X-ray fluorescence analysis (XRF). The surfaces of the samples were observed microscopically and elemental measurements were made using scanning electron microscopy (SEM) (SuperScan SS-550, Shimadzu Corporation, Kyoto, Japan) and energy dispersive X-ray spectroscopy (EDX) (SEDX-500, Shimadzu Corporation).

3.5 Mineralogical analysis

The same samples used for XRF and EDX analyses were further subject to mineralogical study using X-ray diffraction (XRD) (MultiFlex 2kW, Rigaku Corporation, Tokyo, Japan) with Cu–K\(_\alpha\) radiation, with 2\(\theta\) between 5 and 70°.

3.6 Water analyses

We conducted water analyses at site O (seawater) by performing ion chromatography (ICS-1000, Dionex Corporation, Osaka, Japan). At site I (seawater and spring water), we used inductively coupled plasma–atomic emission spectrometry (ICP–AES) (ICP–AES-9000, Shimadzu Corporation).

4. Results

4.1 Needle penetration test

The beachrocks at site O were more indurated than at site I (\(q_u\) of Tables 1 and 2). Moreover, at both sites, the \(q_u\) value of exposed beachrock was higher than that of buried beachrock. These results are similar to those of Vousdoukas et al.\(^4\) Furthermore, to the best of our knowledge, this study is the first to report \(q_u\) of buried beachrock. Only three previous studies from Japan and Scotland\(^11\)–\(^13\) have addressed the mechanical properties of exposed beachrocks.

4.2 Microbial population count

For each sample, marine microbial populations showed viable values (Tables 1 and 2). The populations in beachrock samples at site O and I tended to be smaller than bacterial

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**Table 1** Unconfined compressive strength, \(q_u\) of beachrocks at site O estimated by the needle penetration test, and their microbial populations.

<table>
<thead>
<tr>
<th>Measurement point</th>
<th>Needle penetration test</th>
<th>Microbial population count</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(N_p) N/mm</td>
<td>(q_u) MPa</td>
</tr>
<tr>
<td>Exposed beachrock</td>
<td>80</td>
<td>28</td>
</tr>
<tr>
<td>Buried beachrock</td>
<td>8.9</td>
<td>3.4</td>
</tr>
<tr>
<td>Sand</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Seawater</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

**Table 2** Unconfined compressive strength, \(q_u\) of beachrocks at site I estimated by the needle penetration test, and their microbial populations.

<table>
<thead>
<tr>
<th>Measurement point</th>
<th>Needle penetration test</th>
<th>Microbial population count</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(N_p) N/mm</td>
<td>(q_u) MPa</td>
</tr>
<tr>
<td>Exposed beachrock</td>
<td>8.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Buried beachrock</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Sand</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Seawater</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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Fig. 1 (a) Location map of Okinawa and Ishikawa in Japan, (b) Distribution and (c) view of the studied beachrock at site O, (d) Distribution and (e) view of the studied beachrock at site I.
populations reported from soil ($10^6$ to $10^{14}$ g$^{-1}$), but larger than in the seawater at respective sites, despite the fact that the beachrock is washed by seawater every day. Therefore, this result suggests that the microbiological properties of the beach at these sites affect beachrock formation.

4.3 Urease activity test

About 156 colonies were isolated from the soil near beachrocks at site O. Of these, five colonies changed the solution color to purple after 2 h at 45°C indicating urease activity. Moreover, the pH range of the five samples was 9.0–9.1. In comparison, the pH value of the non-bacterial sample was 7.1.

4.4 Elemental analyses and SEM observation

Results of XRF analyses at site O and site I samples are shown in Figs. 2 and 3, respectively. All samples from site O were composed mainly of CaO, and beachrock samples contained more MgO than adjacent sand (Fig. 2). Meanwhile, site I samples contained many elements, including Al$_2$O$_3$, SiO$_2$, K$_2$O, CaO, FeO, and TiO$_2$ (Fig. 3).

Subsequently, we analyzed sample surfaces by performing SEM-EDX. Figure 4 shows a typical surface condition of exposed beachrock at site O. The elemental composition was measured for different points in the sample. For PO1 to PO3, MgO, Al$_2$O$_3$, SiO$_2$, K$_2$O, CaO, and FeO were detected (Fig. 5). However, PO4 contained mainly CaO and MgO, perhaps because this sample largely contained exposed sand particles. Conversely, a surface of exposed beachrock at site I (Fig. 6) revealed sand (center part of SEM image contained PI2 and PI3) that was covered with cement (PI1 and PI4). Moreover, the main elements of the cement and the sand were Al$_2$O$_3$ and SiO$_2$, respectively (Fig. 7).

4.5 Mineralogical analysis

Site O samples contained the following minerals: Mg calcite (MC), aragonite, and quartz (Fig. 8). In comparison, the minerals found in site I samples were quartz, albite, calcite, and montmorillonite (Fig. 9). MC can be divided into high Mg calcite (HMC) and low Mg calcite (LMC). HMC is a polymorph of CaCO$_3$, containing more than 4 mol% MgCO$_3$, or 1.2 mass%, while LMC contains less than 4 mol% MgCO$_3$.4)
4.6 Water analyses

Results of water analyses at site O and I are presented in Table 3. In addition, this table lists the average global seawater concentrations.15) The chemical composition of seawater at site O was similar to the global average percentage. The Al$^{3+}$ and SiO$_2$ concentrations of spring water at site I were considerably higher than those of seawater collected at the site, and the spring water was acidic (pH 4.7).

5. Discussion

5.1 Beachrock cement

To identify the cement of beachrock at site O, we observed the samples at high magnifications ($\times 1200$, $\times 4800$) by performing SEM-EDX because the results at low magnification ($\times 480$) (Figs. 4, 5) did not reveal sufficient details. The high-magnification results (Fig. 10) showed that the mor-
phology of the microparticulates covered with sand particles was similar to that of HMC. Moreover, the MgCO₃ found in the microparticulates was calculated to be 16–18 mass% (>1.2 mass%) based on the Mg percentage in Fig. 11. Furthermore, the microparticulates were observed on the surface of the buried beachrock as well. Therefore, we conclude that the cement of beachrock at site O is HMC.

For the beachrock at site I, EDX analysis (Fig. 7) showed that this cement contained mainly Al and Si. The Al-containing minerals of the beachrock were determined to be albite and montmorillonite (Fig. 9); however, albite is formed at high temperature and beachrock forms generally at ambient temperatures. Furthermore, the peaks of montmorillonite did not differ greatly between samples (Fig. 9). Therefore, the beachrock cement at site I could be an amorphous phase mainly containing Al and Si.

The cements of beachrocks from around the world are shown in Fig. 12. The figure shows that the cements at 75 out of the 77 sites worldwide were polymorphs of CaCO₃. Among these 75 sites, partial cements contained other materials except for CaCO₃: for example, in Bozcaada Island, Turkey, beachrock cement was mainly HMC, but a few cement mainly composed of Si was observed, too.

Therefore, the beachrock cement at site O is similar to that observed in the majority of the sites globally, whereas the type found at site I is very rare. The site O cement could be considered for constructing man-made rock.

5.2 Formation mechanisms of beachrock

Beachrock cemented by HMC has been reported at 16 sites in the world (Fig. 12), and the formation mechanisms of the beachrocks at 13 sites are shown in Fig. 13.

We focused further investigation of beachrock cements on the influence of precipitation from seawater and/or seawater evaporation (PSW), and on surface microorganisms, which we considered as one biological process (BIOL). This is because (1) PSW is the factor most reported to be related to the formation mechanism of beachrock cemented by HMC (Fig. 13) and (2) microbiological properties may affect beachrock formation at site O (section 4.2 and 4.3). Other effects on beachrock formation are outside the scope of this study and require further consideration in the future.

First, with respect to PSW, Raz et al. reported that to better understand the depositional process of high-magnesian calcitic skeletons, they studied the CaCO₃ precipitates formed from solutions with Mg/Ca ratios ≥4. The ratio Mg/Ca of seawater at site O (Table 3) was approximately 6.3; this ratio satisfies the conditions under which HMC could precipitate. In addition, according to experiments by Kitano et al., sodium citrate and sodium malate favor the precipitation of MC and an increase in concentration of magnesium ion and these organic materials causes formation of Mg-rich calcite. Site O is rich in organic matter, such as sea algae, shells,
corals, and bacteria, which may be the source of citrate and malate.

A second factor—the microbiological effect—was indicated by the urease activity test. We found five colonies of bacteria exhibiting urease activity in the sand near the beachrock at site O (section 4.3). The bacteria stimulates the hydrolyzation of urea, CO(NH$_2$)$_2$. This reaction leads to an increase in the pH value and precipitation of CaCO$_3$, as shown below:22)

$$\text{CO(NH}_2\text{)}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{CO}_3^{2-},$$

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \downarrow.$$  

Moreover, MgCO$_3$ would precipitate with CaCO$_3$. To the best of our knowledge, this is the first time that bacteria exhibiting urease activity have been recorded near beachrock. It is necessary to conduct further tests with the bacteria in the future.

Therefore, our investigation into the formation mechanisms of beachrock has shown that at site O (Fig. 14), the evaporation of seawater and/or the urease activity of microorganisms might have resulted in the precipitation of HMC, leading to formation of beachrock.

Meanwhile, at site I, beachrock seems to have formed by a different mechanism. At this site, the beachrock cement was mainly Al and Si. The Al$^{3+}$ concentration of the spring water was high, at 15.4 ppm, and the pH was 4.7 (Table 3). Al exists as Al$^{3+}$ below pH 4.0, and the concentrations of AlOH$^{2+}$, and Al(OH)$_2^{+}$ increase with pH. Moreover, Al changes into water-insoluble compounds such as Al(OH)$_3$ as the pH increases. Furthermore, Al will not precipitate in an alkaline solution.23)

Therefore, the mixing of spring water with seawater could have led to the precipitation of Al(OH)$_3$ with SiO$_2$ and SO$_4^{2-}$ from seawater and/or spring water between the sand grains in the intertidal zone, thus resulting in the formation of beachrock at site I (Fig. 15).

Furthermore, we considered the relationship of cements and formation mechanisms of beachrocks around the world, including sites O and I (Fig. 16). We found six processes to be reported: PSW; precipitation from fresh water (PFW); CO$_2$-degassing; BIOL; sea-fresh water mixing; physico/chemical factors; and various other mechanisms. Some beachrock sites have developed from more than one mechanism. Moreover, the beachrock examples cemented by calcite tend to have been formed by PFW. In contrast, aragonite and MC tended to have been precipitated from seawater, as beachrock cements. In addition, the beachrocks formed by BIOLs are cemented by HMC, MC and/or Ar.

5.3 Considerations in making artificial beachrock

Formative ages (14C ages) of beachrock samples for site O were reported at 1418–1566 y Cal BP and 1627–793 y Cal BP.24) Conversely, the formative age of beachrock at site I was estimated at 50–60 years ago or more recently, because the beachrock contained a printed board (Fig. 17). However, these timescales are longer than those of existing countermeasures against coastal erosion. Thus artificial beachrock formation methods must also promote rapid solidification.

Based on formation methods observed for site O, artificial beachrock could be cemented by HMC using microorganisms with urease activity, organic matter such as citrate and malate, nutrient sources, CO(NH$_2$)$_2$, artificial seawater and sand. Based on Hata et al.,25) the $q_0$ of some specimens cemented by calcite was observed over 200 kPa for Toyoura
sand columns after a 12-day cultivation period. The materials were *Sporosarcina pasteurii* (a bacteria having urease activity) and solidified solution containing 0.15 mol/L CO(NH2)2 and CaCl2, respectively. For ease of additional consolidation, we conducted a solidification experiment by using *in-situ* bacteria having urease activity and changing the composition of the solidified solution. Moreover, Kawakami et al. reported that a coral sand specimen subjected to wet-dry cyclic conditions in seawater (without adding bacteria) became cemented by aragonite and reached 6 MPa, $q_u$ after 6 months. Therefore, additional endurance could potentially be achieved by conducting both a solidification process using bacteria and an evaporation process.

Hardening of a substrate using HMC as cement material has not been previously reported, while that using calcite has been indicated by Hata et al., Van Paassen et al. The reason for paucity of use of HMC could be that calcite is more stable chemically than MC and aragonite. However, Mg and organic matter are common in the littoral region, and thus it is valuable to consider how to make artificial beachrock cemented by HMC.

However, man-made cement formed by mechanisms operating at site I could be achieved by mixing artificial seawater and solution containing Al3+ and SiO2 concentrations comparable to the spring water. Based on the composition and origin of the beachrock cement at site I (section 5.1 and 5.2), Al(OH)3 was the main constituent. According to the following chemical equation and solubility product (eqs. (3) and (4)), it is efficient to mix the solution containing Al3+ and SiO2 with a small amount of artificial seawater, which can increase pH of the solution. Moreover, repetitive mixing and evaporation would likely strengthen the specimen even further.

$$\text{Al(OH)}_3 \rightarrow \text{Al}^{3+} + 3\text{OH}^-,$$  (3)

$$\text{KSP} = [\text{Al}^{3+}] \times [\text{OH}^-]^3 = 1.3 \times 1033. \tag{4}$$

Finally, with respect to site I, we considered the relationship of cement content of beachrock and $q_u$. Because Al(OH)3 is an amphoteric hydroxide, the cement was dissolved in 1 M NaOH solution for a day. The cement content was calculated from the mass difference between pre- and post-soaking. Results (Fig. 18) indicate that cement content was positively correlated with $q_u$. Therefore, the cement content of beachrock is an important parameter with respect to strength increase.

### 6. Conclusions

We performed needle penetration tests, determined viable bacterial counts, conducted elemental and mineral analyses of beachrocks and sands, and analyzed seawater and spring water adjacent to the beachrock samples to investigate the formations of beachrocks at Okinawa and Ishikawa in Japan. These results revealed that formation mechanisms varied between the sites.

At Okinawa, the evaporation of seawater and/or urease activity of microorganisms may have resulted in precipitation of HMC, leading to formation of the beachrock.

At Ishikawa, mixing of spring water with seawater could have led to the precipitation of Al(OH)3 with SiO2 and SO42- from seawater and/or spring water between sand particles in the intertidal zone, thus resulting in formation of the beachrock.

### Acknowledgement

This research was supported by JSPS Grant-in-Aids (21300326 and 24-1036). We are grateful to Suguru Shimazaki and Nao Aoki of Hokkaido University for conducting the urease activity tests.

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