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Environment Improvement in the Sea Bottom by Steelmaking Slag†

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Abstract:

The applicability of steelmaking slag was examined to improve the bottom sediments in several sea areas. The experimental results showed that massive steelmaking slag controlled the occurrence of sulfide, and that the materials were available as a submerged embankment material, which can be used for a base of algae and benthonic organisms. It is also found that the granules of the steelmaking slag can be an effective base and can supply nutrients for attached algae.

1. Introduction

In the inner bays and coastal districts in Japan, many sea areas have vertical seawalls installed after land reclamation and suffer from eutrophication due to the inflow of domestic wastewater from rivers, requiring environmental restoration. In these areas, problems such as red tide and blue tide, as well as decline in marine resources, have emerged. Projects to restore the environment have often used natural sand and stones, but the extraction of these natural resources may itself destroy the environment.

The authors are therefore examining ways of using steelmaking slag to improve the coastal environment without destroying nature[1]. This paper outlines some examples.

2. Utilization of Massive Steelmaking Slag

2.1 Verification Test of Sulfide Generation Inhibiting Effect on Enclosed Coastal Areas

Massive quantities of steelmaking slag were placed at the coastal test site of Tokai Univ. at Orido, Shimizu-ku, Shizuoka, Japan in order to verify the effect of the slag on inhibiting sulfide generation. A 12 *l* container of steelmaking slag was installed at the bottom of the sea, and the overlaying water and interstitial water in the slag were collected and the sulfide concentration was measured. Two months after installation, sulfide was not detected in the section where the steelmaking slag was installed, whereas in the granite and concrete sections used as a reference, 0.2–0.25 mg/*l* of sulfide

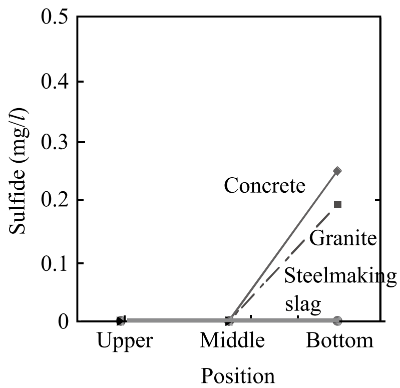

Fig. 1 Sulfide concentrations in overlying water, middle and bottom interstitial water in concrete, granite and steelmaking slag

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was detected in the bottom interstitial water as shown in **Fig. 1**[2]. This result shows that steelmaking slag inhibits the generation of sulfide which damages living organisms, and improves the sea bottom. It is considered that the Ca ions that liquate out of steelmaking slag increase the hydrogen ion concentration in interstitial water, decreasing the activity of sulfate-reducing bacteria[3], and that the iron in slag reacts with sulfide to form iron sulfide.

2.2 Bottom Sediment Improvement Test under Oyster Raft

Oyster production in Hiroshima Pref. is the largest in Japan[4], but the problem of deterioration of bottom sediment due to oyster farming has been pointed out. One of the major causes is thought to be the organic load such as oyster excrement and fallen oyster shells[5].

In this test, as shown in **Fig. 2**, 20 *l* bottomless containers containing massive steelmaking slag of 30–100 mm in diameter were placed on the sea bottom (20 m in depth) under an oyster raft installed off Takata Harbor in Etajima Bay in Hiroshima. Granite of similar diameter was also put on the sea bottom for comparison. **Figure 3**

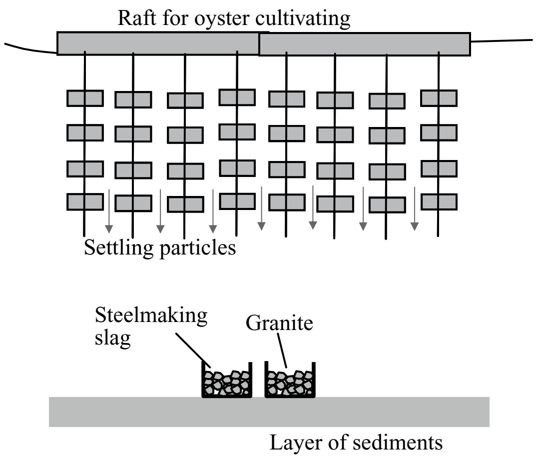

Fig. 2 Scheme of massive steelmaking slag under the raft for oyster cultivating

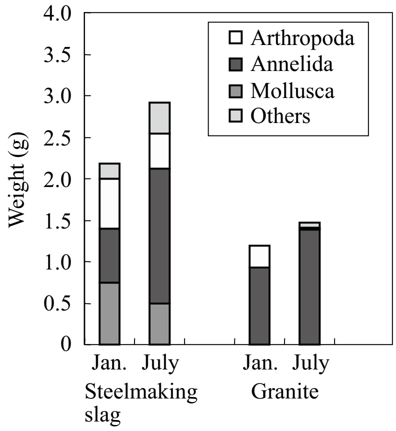

Fig. 4 Wet weights of benthos observed on January and July in 2006

shows the time changes of (a) sulfide and (b) oxidation reduction potential. There was less sulfide in the slag section than in the granite section in both the upper- and middle-layer water, whereas the oxidation reduction potential was higher, suggesting that the steelmaking slag changed the bottom sediment to aerobic under the oyster raft.

Figure 4 shows the wet weights of benthos. The wet weights were heavier in the slag section than in the granite section, and the ratio of Mollusks and Arthropods was higher. Conceivable causes are the steelmaking slag that keeps the bottom sediment in an aerobic environment and the formation of a space suitable for living organisms in the gaps in the gravel.

These findings suggest that massive steelmaking slag controls the deterioration of bottom sediment.

2.3 Utilization as Submerged Embankment Material on Artificial Shoal

A shoal model was created using steelmaking slag blocks in the sea area off Innoshima, Hiroshima in March 2002. **Figure 5** shows the plan drawing[6]. As the submerged embankment material for the shoal, mas-

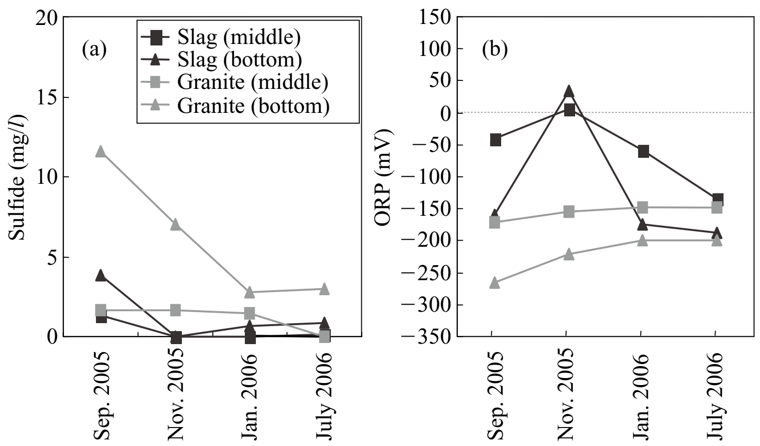

Fig. 3 Time changes of (a) sulfide and (b) oxidation reduction potential in interstitial water

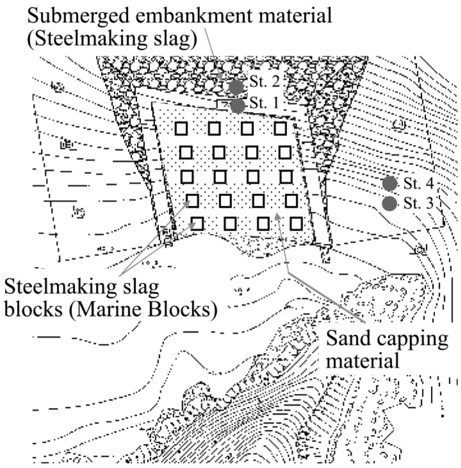

Fig. 5 Plan of coastal environment improvement test using steelmaking slag

sive steelmaking slag of less than 80 mm in diameter was placed surrounding the covering sand over an area of approximately 30 m × 20 m. After land preparation, the condition of adhesion of animals and plants to the steelmaking slag was periodically observed to verify the sessile characteristics of steelmaking slag when used as a submerged embankment material.

Enteromorpha intestinalis, *Hypnea charoides* Lamouroux, and other kinds of seaweed were observed four months after installing the submerged embankment material, and Sargasso and Rhodophyta, as well as young and adult fishes, were observed eleven months later as shown in **Photo 1**[6]. **Figure 6** shows the cell numbers of algae attached to the steelmaking slag and natural stones[6]. The identified cell numbers of algae attached to the steelmaking slag used as a submerged embankment material (St. 1 and St. 2) were larger than those on the natural stones (St. 3 and St. 4). Conceivable causes are the existence of a large quantity of fine irregularities on the surface of the steelmaking slag and the possibility of adhesion of algae due to the supply of

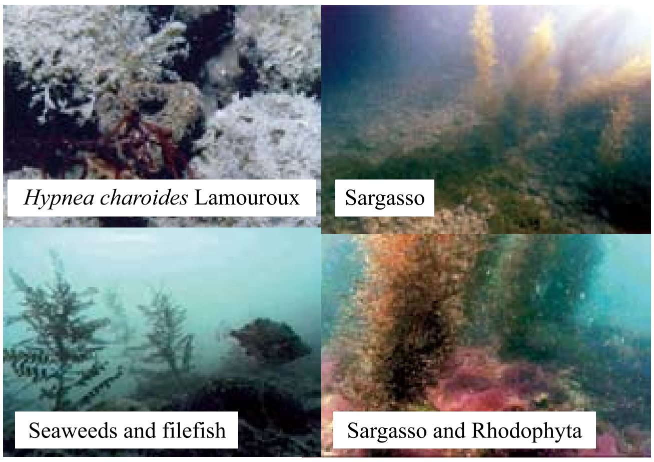

Photo 1 Seaweeds observed on steelmaking slag

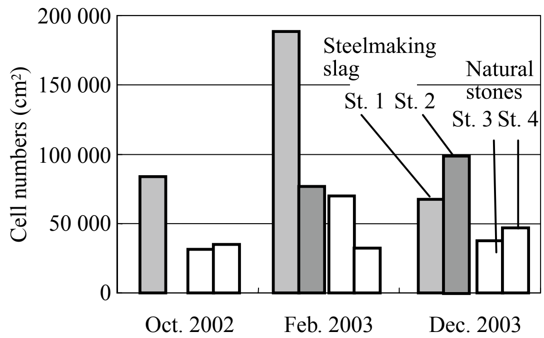

Fig. 6 Cell numbers of attached algae on steelmaking slag and natural stones

Fe, P, and Si[7].

In general, shoals function as (1) seaweed cultivation areas, (2) benthonic organism habitats, and (3) swarming and growing fields for young and adult fishes. The results of this test, as well as the tests described in Sections 2.1 and 2.2, verified that the steelmaking slag provides all of these three functions, suggesting that the slag helps to purify the water and improve the bottom sediment. These results demonstrated steelmaking slag was a suitable materials for shoals.

3. Utilization of Granular Steelmaking Slag

3.1 Adhesion Characteristics of Phytoplankton

The grain size, surface shape (groove), and the change in adhesion characteristics depending on the hydrogen ion concentration in solution were examined using *Nitzschia* sp. as a sample microbe to examine the adhesion characteristics of phytoplankton (**Fig. 7**). No significant difference due to grain size was observed in the test, in which glass beads of 0.1–10 mm in diameter were used.

The surface shape was examined using a polypropylene sheet after polishing its surface with sandpaper. Three types of sandpaper, #60: 212–300 μm; #120: 90–125 μm; and #320: 34–94 μm, were used in the test

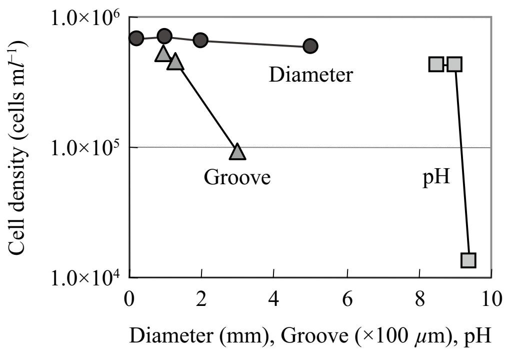

Fig. 7 Characteristics of adhesion in phytoplankton

to compare the quantity of deposit. As a result, a smaller groove showed greater adhesion.

NaOH was used to control the hydrogen ion concentration in the artificial seawater in the test to examine the influence of the hydrogen ion concentration. As a result, the multiplication of adhering phytoplankton was controlled when the pH value exceeded 9.4. In general, the multiplication range of phytoplankton is considered to be pH 6.3–10[8], and it was confirmed that *Nitzschia* sp. also multiplied when the pH was below 9.4.

It is therefore suggested that the adhesion characteristics of phytoplankton do not change significantly with the difference in adhesion surface area (grain size), but that the surface shape and hydrogen ion concentration have a substantial influence.

3.2 Adhesion to Steelmaking Slag

In order to examine the characteristics of phytoplankton that adheres to steelmaking slag, dephosphorization slag, decarbonization slag, and steelmaking slag with carbonic acid were used and the quantity of adhering phytoplankton was examined (**Fig. 8**). For comparison, glass beads and blast furnace slag of 2 mm in diameter, as well as blast furnace granulated slag of 1 mm in diameter, were used. The cell density of phytoplankton was low in the decarbonization slag and blast furnace slag, which was considered to be attributable to the influence of the hydrogen ion concentration because the hydrogen ion concentration in these solutions was high compared with the glass beads. Meanwhile, the dephosphorization slag and steelmaking slag with carbonic acid showed higher hydrogen ion concentration than glass beads, but the cell density was the same or higher, which was considered to be attributable to the surface shape because the surface of steelmaking slag was more rough than that of the glass beads.

Next, the dephosphorization slag and glass beads were subjected to microscopic analysis to evaluate the adhesion of diatom on the surface of steelmaking slag. The microscopic analysis revealed that diatom, as well as adhesive polysaccharide, covered the surface of the steelmaking slag and the existence of an orange-colored substance, which was not observed on the glass beads, was confirmed on the inside (**Fig. 9**). This substance was identified by XRD as an iron compound (FeO(OH)) (**Fig. 10**). Accordingly, it is suggested that Fe derived from steelmaking slag promoted the adhesion of diatom.

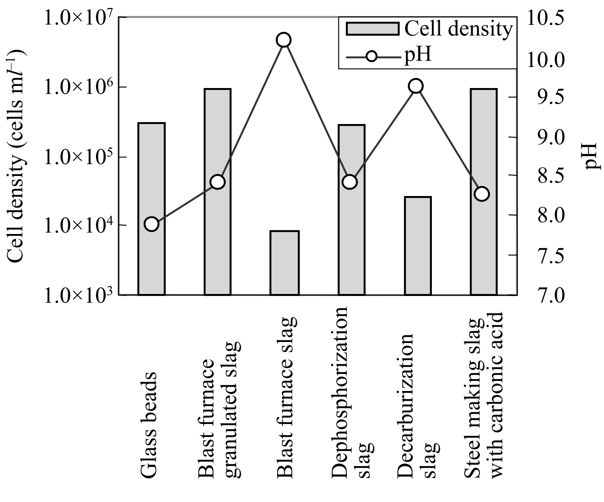

Fig. 8 Adhesion of phytoplankton to slag

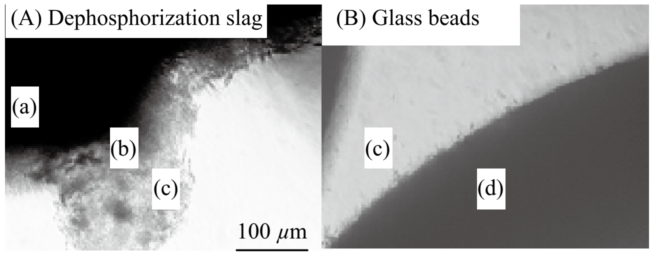

Fig. 9 Analysis of adhesion of the diatom on the steelmaking slag by microscope ((A); Dephosphorization slag, (B); Glass beads) ((a) steel making slag, (b) FeO(OH), (c) the diatom, and (d) glass beads)

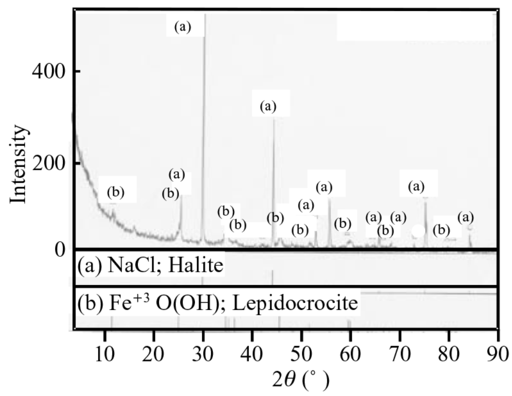

Fig. 10 XRD of precipitate from dephosphorization slag ((a) NaCl and (b) FeO(OH))

According to a report by Nakamura et al.[7], a similar investigation was made to examine the multiplication effect of slag-derived Fe on phytoplankton, because slag-derived Fe had already been shown to promote phytoplankton multiplication.

3.3 Effect of Constituents of Steelmaking Slag

The effect of slag constituents was investigated to examine the chemical influence of steelmaking slag on the multiplication of phytoplankton. Culture solutions were prepared for the test by removing iron (Fe) and phosphorus (P) from the Guillard medium[9] used for phytoplankton culture, and the growth of phytoplankton was examined by using 15 m*l* of culture solutions for 1 g of dephosphorization slag and glass beads of 2 mm in diameter, respectively. As a result, the multiplication of phytoplankton on dephosphorization slag in the culture solution without Fe was similar to that in a culture solution containing Fe. On the other hand, multiplication of phytoplankton on dephosphorization slag was not observed in the culture solution without P. According to Ito et al.[10], the maximum elution of P from the slag was 2.2 mg-PO_4^{3-}/g-slag. According to a report by Arita et al.[11], the effect of Fe and P as nutrients for phytoplankton by addition of decarburization slag has been confirmed. In both reports, however, the grain sizes were as small as 0.05 mm and 0.02 mm; therefore, the effect of steelmaking slag of 2 mm in diameter is considered to be small because the elution amount of P is small.

Meanwhile, Fe showed a phytoplankton multiplication effect even with the grain size of 2 mm.

4. Conclusions

Several tests were conducted in actual sea areas to verify the effect of steelmaking slag on improving the bottom sediment in sea areas. The following findings were obtained.

(1) Massive steelmaking slag controls the generation of sulfides in enclosed sea areas and oyster farms and maintains the oxidation reduction potential at a high level, thus improving the bottom sediment. Massive steelmaking slag was shown to function as a submerged embankment material with excellent sessile characteristics on artificial shoals.

(2) The adhesion of phytoplankton to granular steelmaking slag depends on the surface shape and hydrogen ion concentration. Fe eluted from steelmaking slag is thought to promote the adhesion and multiplication of phytoplankton.

As a result, granular steelmaking slag could be used as a phytoplankton adhesion base or as a source of nutrients.

An artificial shore off Innoshima, Hiroshima Prefecture, was created as part of a project supported by Hiroshima Pref. in 2001 through the cooperation of Hiroshima Pref. and many other people. The bottom sediment improvement test under the oyster raft was conducted as a project supported by the Etajima Bay Regeneration Committee (Secretariat: Fishery Promotion Section, Industrial Division, Etajima City) through the generous cooperation of those involved. The authors are grateful to Professor Tamiji Yamamoto at the Graduate School of Biosphere Sciences, Hiroshima Univ., for his kind information about the phytoplankton culture method.

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