Improvement of Marine Environment Using "Marine StoneTM" Made of Steelmaking Slag^{\dagger}

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Abstract:

To evaluate the sulfide reduction effect of "Marine Stone", which are made of steelmaking slag, field experiments were conducted in Fukuyama inner harbor, where sulfur odors caused by hydrogen sulfide containing gas generated from the sediments is an issue for local citizen. "Marine Stone", 5 500 tons in total, were applied on the bottom sediments to suppress the odor production. In "Marine Stone" applied plot, dissolved sulfide concentrations in the interstitial water were suppressed drastically compared to those in the control plot, and the effect has lasted for about two years. It was supposed that dissolved sulfide may have reacted with Fe ions eluted from "Marine Stone" and insolubilized. The numbers of species and individual numbers of macrobenthos increased in the experimental plot. These results imply that capping deteriorated sediments with "Marine Stone" can effectively improve the water and sediment quality of coastal areas.

1. Introduction

In enclosed coastal seas and waters where silty sediment has accumulated, an environment suitable for growth of sulfate-reducing bacteria forms as a result of stagnation of the water mass, oxygen deficiency due to decomposition of organic matter, etc., and hydrogen sulfide is generated^{1,2)}. Hydrogen sulfide not only has adverse effects on aquatic organisms due to its high toxicity, but is also a main cause of bad odor.

Several studies have investigated steelmaking slag, which is a byproduct of the steelmaking process, as a remediation technique for marine environments. Japan produces approximately 15 million tons/yr of steelmaking slag, which is used as roadbed materials and civil construction and the like³⁾. However, high value-added applications utilizing the physical properties and composition of steelmaking slag have not been adequately developed. Application as a countermeasure for denudation of rocky shores⁴⁾ and in improvement of bottom sediments in closed bodies of water have been reported in recent years^{5,6)}, but adequate study has not been devoted to bottom sediment improvement for silty sediment in actual waters where large amounts of hydrogen sulfide generate and cause malodor.

Therefore, a technology for suppressing the dissolved sulfides eluted from silty sediment, which is a cause of bad odor, was developed by using a steelmaking slag product called "Marine StoneTM" (hereinafter, Marine Stone). As the first step, laboratory-scale tests were conducted using silty sediment from the waters in Fukuyama inner harbor⁷⁾ in Fukuyama City, Hiroshima Prefecture (Fig. 1), where hydrogen sulfide odor has become a problem, and a basic study of the hydrogen sulfide suppression effect of Marine Stone was carried out⁸⁾. As the next step, field experiments⁹⁾ were

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Fig. 1 Location of Fukuyama inner harbor⁹⁾

conducted in the actual waters at Fukuyama inner harbor. This report describes the effects that were verified as a result of those tests.

2. Experimental Method

2.1 Construction

Marine Stones were constructed in the test Site A (area: 432 m²) in August 2011 as shown in **Fig. 2**. The chemical composition of the Marine Stones (produced by JFE Steel Corporation, West Japan Works) used in this test is shown in **Table 1** (MS 1). The Marine Stones were loaded on a crane barge, and laid by using a clamshell dredger. First, a 35 cm thick bottom layer of Marine Stones with a size of 5–10 mm was constructed, after which a 35 cm top layer of Marine Stones with a size of 10–25 mm was constructed. This area was called Marine Stone test site (hereinafter, "Site") A.

Next, in July 2012, the second construction was carried out in Site B and Site C (Fig. 2, total area: 3510 m^2) by the same procedure described above. The chemical compositions of the Marine Stones used are shown in Table 1. In Site B, both the bottom layer material and the top layer material were the same as in Site A. On the other hand, in Site C, MS 1 was used as



Fig. 2 Location of "Marine Stone" construction area⁹⁾

Table 1 Chemical composition of "Marine Stone" 9) mass%

	T.Fe	SiO ₂	CaO	Al ₂ O ₃	MnO	MgO	TiO ₂
MS 1	17.5	29.3	33.0	6.0	8.7	4.9	1.2
MS 2	20.7	12.7	42.2	3.1	2.7	6.2	0.5



Fig. 3 Cross section diagrams of monitoring sites from July 2012 $\text{onward}^{9)}$

the bottom layer material, and MS 2 (produced by West Japan Works) with a size of 30–50 mm was used in the top layer material. In a previous study, the authors showed that MS 2 plays a role as an adhesion substrate for seaweed and benthos in different waters¹⁰). Therefore, this material was selected for the top layer material, expecting the possibility of adhesion of macrobenthos in the waters in this study. In all three sites, the thickness of the top layer and bottom layer materials was 35 cm each, for a total thickness of 70 cm.

2.2 Monitoring Sites after Construction

The generated gas, water quality, macrobenthos, etc. were investigated after the first round and second round of construction. A cross section of the positions of the monitoring sites after the second round of construction is shown in **Fig. 3**. Site A (origin: 0 m), Site B (65 m toward the harbor entrance from the origin) and Site C (134 m toward the harbor entrance) were selected as the monitoring sites, and Control plots were set at 100 m from the origin toward the bay head and 244 m toward the harbor entrance, i. e., sea side.

2.3 Investigation Method

2.3.1 Bottom sediment interstitial water

Sampling of the interstitial water was performed after 2 weeks (July 2012), 12 weeks (October), 19 weeks (November), 21 weeks (December), 30 weeks (February 2013), 37 weeks (March), 41 weeks (April) and 46 weeks (June) after the second test. Sampling of the interstitial water in the test sites was performed by a diver, who connected a TygonTM tube to a ceramic air stone buried in advance at a depth of 5–10 cm from the Marine Stone surface during construction by using a syringe. In the control plots, core samples of the bottom sediments were taken with an acrylic pipe having a diameter of 10 cm, and the sediments were sampled from a position 5–10 cm below the surface of the bottom sediments.

The pH, oxidation-reduction potential (ORP) and dissolved sulfides of all of the samples were measured by using an IM-22P (Pt reference electrode) manufactured by DKK-TOA Corporation and Kitagawa's type detector tubes (200SA, 200SB) manufactured by Komyo Rigaku Kogyo K. K., respectively. In addition to these measurements, following the second round test, the dissolved oxygen concentration was also measured by the Winkler method. Interstitial water of the bottom sediment samples taken by a diver was used for the measurements of dissolved sulfide and dissolved oxygen concentration after centrifugation.

2.3.2 Overlying water

Simultaneously with sampling of the interstitial water, the overlying water approximately 5–10 cm above the surface of the bottom sediments was sampled. Sampling was performed from the ship by a hand pump connected to a TygonTM tube. The pH, ORP, dissolved sulfide and the dissolved oxygen concentration of these specimens were measured by the same methods as those used for the interstitial water of sediments.

2.3.3 Generated gas and its composition

In September, October and December of 2011 and July and October of 2012, the gas which evolved naturally from the sea bottom was captured by chambers installed at the sea bottom, and the volume of collected gas were measured. The gas discharged in a shaking test of the bottom sediment was also measured in December 2012. As samples of the bottom sediments in the test sites, mud in the gaps between Marine Stone particles was collected by a diver. The sediment in the control plots was collected by core sampling. Approximately 1 000 mL of the bottom sediment sample was placed in a 2 L wide-mouthed bottle and sealed, the wide-mouthed bottle was shaken with a shaking machine (manufactured by TAITEC Corporation) at a rotation speed of 200 rpm and amplitude of 5 cm for 6 hr. The hydrogen sulfide concentration in the gas in the container was then measured with a detector (manufactured by RIKEN Keiki Co., Ltd.) and the concentrations of dimethyl sulfide and methyl mercaptan were measured with a gas measurement detector tube (Gastech Corporation).

2.3.4 Macrobenthos

Quantitative analyses of macrobenthos were performed in February, March, April and June of 2013 after the second round test. Bottom sediments with an area of 25 cm×25 cm and a depth of 10 cm were sampled by a diver using a stainless steel frame (area: $25 \text{ cm} \times 25 \text{ cm}$, depth: 15 cm), and the number of species, number of individuals and wet weight of the macrobenthos sieved with a mesh of 1 mm were measured.

3. Results

3.1 Water Quality

3.1.1 Interstitial water

The results of the measurements of dissolved sulfide concentration after the second test are shown in Fig. 4 (a). The dissolved sulfide concentration was high (60-400 mg/L) in the control plots. In contrast, it was markedly low ranging from below the detection limit (0.5 mg/L) to 20 mg/L in the test sites. Moreover, the dissolved sulfide concentrations in Sites B and C in the second test were in approximately the same level. The ORP of the bottom sediment were shown in Fig. 4 (b). In the first round test, the ORP in the test sites showed a clearly higher values, -20 to +100 mV, in comparison with the control plots. A decreasing trend could be seen from 2 to 8 weeks, but increased during winter (December). In the control plots, the ORP was low, being around -200 mV, regardless of the timing of the measurements. In contrast to this, while seasonal changes could be seen in the test sites, it was high in comparison with the control plots, being -20 to +100 mV in Site A and 0 to +220 mV in Sites B and C.

The values of the dissolved oxygen concentration are shown in Fig. 4 (c). From autumn through winter, the issolved oxygen concentration of the interstitial water was higher in the slag construction area than in the control plots.



Fig. 4 Temporal changes of (a) dissolved sulfide, (b) Eh (ORP) and (c) DO in interstitial water in test area and control plots



Fig. 5 Temporal changes of (a) dissolved sulfide, (b) Eh (ORP) and (c) DO in overlying water in test area and control plots

3.1.2 Overlying water

The results of measurements of the dissolved sulfide concentration, ORP and dissolved oxygen concentration in the overlying water of the test sites and control plots are shown in **Fig. 5** (a) through (c), respectively. Almost no dissolved sulfide was detected at either the test sites or the control plots, regardless of the measurement dates. The ORP and dissolved oxygen concentration showed tendencies to decrease in summer and increase in the winter no differences were observed between the test sites and the control plots, but the values tended to be lower at the bay head and higher on the sea side, which was consistent with the results of measurements in 2009¹¹.

3.2 Gas Generated from Bottom Sediments

The results of the measurement of gas concentration in the container in the shaking test of the sampled bottom sediments in December 2012 were shown in **Fig. 6**. In the control plots, the hydrogen sulfide gas concentration was 300 ppm at the bay head side and 1 200 ppm at the sea side, but in contrast, the concentration in the test sites was below the detection limit (< 1 ppm). Similarly, in the control plots, the maximum concentrations of dimethyl disulfide and methyl mercaptan were 70 ppm and 10 ppm, respectively, Contrariwise, were below the detection limits in the test sites. (The detection limits for hydrogen sulfide gas, dimethyl disulfide and methyl mercaptan are 0.1 ppm, 0.36 ppm and 0.25 ppm, respectively.) These showed



Fig. 6 Hydrogen sulfide, methyl mercaptan and dimethyl disulfide concentration in bottle after shaking in December 2012⁹⁾



Fig. 7 Species number, individual numbers and wet weight of macrobenthos observed in and on sediment in February 2013

that generation of hydrogen sulfide and other malodorous components in the bottom sediments were remarkably suppressed.

3.3 Adhesion of Macrobenthos

The number of species, number of individuals and wet weight of macrobenthos in February 2013 were shown in **Fig. 7**. In the control plots, 1 or 2 species of Annelida were observed, and the number of individuals and wet weight were 20–150 individuals and 0.5– 1.0 g per 0.1 m², respectively. In the test sites, 3–6 species of Annelida, Mollusca, etc. were observed, and the number of individuals and wet weight were 500–1 400 individuals and 5–23 g per 0.1 m². The organisms adhering to lumps of Marine Stones sampled in Site C is shown in **Photo 1**. As shown in this photo, crabs and a transparent sea squirt (*Ciona savignyi*) adhering to the surface of Marine Stones were observed in Site C.



Photo 1 Macro benthos observed on C-plot in February 2013

4. Discussion

4.1 Effect of Suppressing Dissolved Sulfides in Bottom Sediments

When sulfide-reducing bacteria decompose organic matter in bottom sediment under anaerobic conditions, hydrogen sulfide is formed by the reduction of sulfide ions (SO₄^{2–}), as shown in Eq. $(1)^{12}$.

$$SO_4^{2-}+2CH_2O+2H^+ \rightarrow H_2S+2CO_2+2H_2O...(1)$$

In water, hydrogen sulfide exists mainly as the hydrogen sulfide ion (HS⁻), which partially elutes from the bottom sediments into the overlying water. In the field tests⁸⁾ in this report, which was based on the laboratory tests, it was shown that the effect of Marine Stone in suppressing dissolved hydrogen sulfide in interstitial water and the amount of generated gas continued after approximately 2 years. Moreover, an effect of suppressing hydrogen sulfide gas in the generated gas was also confirmed. Using the EPMA analysis, Hayashi et al¹³⁾. performed element mapping of the surface of Marine Stone after the reaction between the Marine Stone and an aqueous solution of sodium sulfide, and reported good agreement between the distributions of sulfur (S) and iron (Fe) at the surface of Marine Stone. Furthermore, based on the results of non-reflective X-ray diffraction analysis and synchrotron radiation analysis, it has been estimated that formation of iron sulfide and elemental sulfur occurs. Similarly, in the present research, there is a possibility that Fe from the Marine Stone is eluted in the bottom sediment, and this contributes to suppression of sulfides in the bottom sediments by formation of iron sulfide and elemental sulfur. In the future, it will be necessary to clarify whether Fe is eluted in the bottom sediment or not by a detailed investigation.

On the other hand, in the overlying water, no difference in dissolved sulfides, etc. was observed between the test sites and the control plots. As the reason for this, because tides have a strong effect on advection and diffusion of sea water in actual seas, it seems difficult to detect the eluted sulfide because the bottom sediment was improved.

4.2 Influence on Dissolved Oxygen Concentration

In this test, as shown in Fig. 5 (c), recovery of dissolved oxygen from fall through winter was observed after the oxygen deficiency from spring through summer. At the bay head of enclosed bodies of water such as Tokyo Bay, Osaka Bay, etc., the bottom water becomes oxygen deficient in summer due to the formation of a thermocline in that season, and the oxygen concentration increases in winter as a result of a vertical mixing. Similar seasonal variations are also thought to occur in Fukuyama inner harbor. From fall to winter, when the dissolved oxygen concentration of the overlying water increased, there was no increase in the dissolved oxygen concentration in the interstitial water of the bottom sediments in the control plots, as shown in Fig. 4 (c). As the reason for this, since a large amount of dissolved sulfide exist in the interstitial water in the bottom sediments in the control plots, it is thought that dissolved oxygen at the sea bottom is consumed by hydrogen sulfide (Eq. (2)).

$$2H_2S+O_2 \rightarrow 2H_2O+2S$$
(2)

In contrast, in the test sites, the dissolved oxygen concentration in the interstitial water of the bottom sediment increased. This is thought to occur because the consumption of dissolved oxygen by hydrogen sulfide by the reaction in Eq. (2) was suppressed due to the low concentration of dissolved sulfides in the test sites. The increase in the dissolved oxygen concentration from fall to winter is attributed thought to be to the influence of comparatively high seawater exchange between the interstitial water of the Marine Stones and the overlying water, which occurs because the large size of the Marine Stone used in the top layer material makes it possible to hold a large amount of interstitial gap between the Marine Stone particles.

4.3 Influence on Habitat of Macrobenthos

In comparison with the control plots, the amount of adhering organisms inhabit in the test sites in winter. The reasons for this are thought to be 1) the increase in the dissolved oxygen concentration in the interstitial water in the test sites, and 2) the result that the surface of the Marine Stone and the gaps between the gravel became habitats for macrobenthos. Where, 2) is concerned, Marine Stone also functions as a substrate for adhesion of marine organisms in addition to the bottom sediment improvement effect. Among the test sites, the highest individual number and wet weight were both observed in Site C, which was located furthest to the sea side. As described in section 3.1.2, in comparison with the head of the bay, the overlying water on the sea side tended to have a higher ORP and dissolved oxygen concentration, and thus is thought to form a suitable living environment for macrobenthos.

The transparent sea squirt (*Ciona savignyi*) observed inhabiting in this area in February 2013 is a type of filter feeder that has a function of removing suspended solids by filtering sea water¹⁴⁾. In addition to a decrease in the wastewater inflow load due to the construction of a new stormwater reservoir by Fukuyama City in April 2014, the bottom improvement area was also expanded to a scale of 6.7 ha by Hiroshima Prefecture in FY 2015. Thus, due to the increase in the exposure period and the larger surface area of Marine Stones, the possibility of improvement of the suspended matter purification capacity due to an increase in the number of adhering filter feeders such as *Ciona savignyi*, etc. and an expansion of their habitats is expected.

4.4 Applicability of Marine Stone as Hydrogen Sulfide Suppression Material for Silty Sediment

Regarding the bottom sediment improvement effect, in addition to the fact that Marine Stone does not cause the environmental destruction associated with the extraction of natural materials from lands, etc., the results of the laboratory experiments⁸⁾, the present report has clearly demonstrated that Marine Stone also has an advantage of chemical reactions to oxidize/ detoxify dissolved hydrogen sulfide. These effects are coming from iron contained in Marine Stone, and thus cannot be expected with natural materials. Figure 8 illustrates a schematic diagram of the behaviors of sulfur and iron between bottom water and bottom sediments based on the results obtained in the present study and other relating papers. It also shows that Marine Stone functions as a substrate for macrobenthos by providing dissolved oxygen through suppressing hydrogen sulfides.

Based on these aspects, it concluded that application of Marine Stone in capping of silty sediments containing hydrogen sulfide is useful for improvement of environmental quality in enclosed coastal seas.

5. Conclusion

A field experiment to demonstrate a technology for reduction of hydrogen sulfide in silty sediment by constructing Marine Stone was conducted at Fukuyama inner harbor, where silty sediment with high sulfide content caused a problem of malodor. In August 2011,



Fig. 8 Scheme of reaction of iron and sulfur

Marine Stone was laid in an area of 430 m^2 , followed by construction in an area of 3510 m^2 in July 2012. A monitoring of various environmental parameters at the test sites and control plots was carried out after the constructions, and the following results were obtained.

1) In the test sites, the concentration of dissolved sulfides in the interstitial water of the bottom sediments was reduced markedly in comparison with the control plots. Increases in the oxidation-reduction potential and dissolved oxygen were also observed, and those effects continued through the study period of approximately 2 years. It was considered to be due to the formation of iron sulfide, etc. by reaction between the dissolved sulfides and the iron eluted from the Marine Stone.

2) In comparison with the control plots, the volume of gas generated from the silty sediment decreased in the test sites. It was also proven by the shaking test of the sediment in which gas generation also decreased.

3) However, no difference between the test sites and the control plots was observed in the water quality of the overlying water and the layer above it. This was attributed to the movement of sea water driven by tidal excursion.

4) Increase in the dissolved oxygen concentration in the interstitial water was observed in the test sites from fall to winter, but was not observed in the control plots. This may be due to suppression of consumption of oxygen that is supposed to be consumed by dissolved sulfides at the test sites. Seawater can permeate into the space between the Marine Stone grain because of the large grain size of the Marine Stone.

5) Adhesion of a transparent sea squirt (*Ciona savignyi*) and spionids, etc. to Marine Stone was observed at the test site located furthest to the sea side (harbor entrance side) in winter to spring. In addition to the chemical function of suppressing hydrogen sulfide and increase in dissolved oxygen in the bottom water, Marine Stone can functions as a substrate for marine organisms to adhere on. Based on the above results, it is concluded that

Marine Stone is effective to improve sediment quality through suppression of sulfide generation that causes malodor and provide substrate for benthic animals.

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