A Field Experiment of Sulfide Reduction in Silty Sediment Using Steel-making Slag

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Hydrogen sulfide is often generated through sulfate reduction under anaerobic conditions in enclosed coastal seas. It is highly toxic, depletes oxygen and forms blue tides. To evaluate the sulfide reduction effect of steel-making slag, we conducted field experiments in Fukuyama inner harbor, where people have suffered from odors caused by gasses including hydrogen sulfide generated from the sediments. We placed steel-making slag on the sediments, and monitored the quality of interstitial water in the sediments and the overlying water. Hydrogen sulfide gas was also collected and measured. Dissolved sulfides in the interstitial water of the steel-making slag construction area were suppressed to below 5 mg/L (as sulfur), while levels ranged from 100 to 350 mg/L in control plots; this reduction lasted for about 2 years. It was assumed that Fe ions eluted from steel-making slag may have reacted with the sulfide. Species number and individual numbers of macrobenthos increased in the steel-making slag construction area. The results imply that capping deteriorated sediments with steel-making slag can effectively improve water and sediment quality of coastal areas.

KEY WORDS: steel-making slag; dissolved sulfide; Fukuyama inner harbor; hydrogen sulfide; sediment; coastal environment; sand capping; sulfate reduction.

1. Introduction

In enclosed coastal seas water stagnates for extended periods of time, resulting in decomposition of organic material. This causes oxygen depletion, creating a reducing environment in which sulfate-reducing bacteria generate hydrogen sulfide, a highly toxic compound that has adverse effects on aquatic organisms and causes a foul odor.1,2) Japan produces approximately 40 million tons of iron and steel-making slag each year, and has achieved a slag reuse rate approaching 100%. The iron-making process produces 25 million t/yr of blast furnace slag, which is already used in high value-added applications. The steel-making process generates about 15 million t/yr of steel-making slag. Although 60% of this is used in roadbed materials and civil construction, technologies that enable high value-added use while taking advantage of the physical properties and chemical composition of the slag have not been adequately established.3)

The authors previously investigated sulfide reduction in sea areas as a potential high value added use of steel-making slag.4,5) Additionally, dissolved sulfides in interstitial water were confirmed to decrease in response to laying steel-making slag in actual coastal waters.6) More recently, we clarified the mechanism of sulfide reduction by iron eluted from steel-making slag in laboratory experiments.7–10) However, these studies were limited to laboratory-scale or small-scale tests in actual waters, and no practical scale examples of sulfide reduction in high organic sediments in response to steel-making slag have been conducted to date.

Therefore, we began a study of the reduction of dissolved sulfides and suppression of the formation of hydrogen sulfide gas by placing steel-making slag on sediments (capping) or mixing the slag into the sediments. In a previous study,4) we confirmed that the concentration of dissolved sulfide in the interstitial water of sediments and water directly overlying the sediments decreased when steel-making slag was placed on or mixed in mud sampled from aquatic systems. We also found that this suppressed generation of hydrogen sulfide gas to the gas phase, and that these effects continued for at least 6 months. In the present study, we conducted demonstration tests in actual waters as a next step. We report here the effects obtained by conducting a capping test using steel-making slag from the Fukuyama inner harbor, which is located in the back part of the bay at Fukuyama Port in
Fukuyama, Hiroshima Prefecture, Japan.

2. Methods

2.1. Outline of the Experimental Area

Field experiments were carried out in the Fukuyama inner harbor, which is a canal-shaped area with a width of 0.1 km and a length of 2.2 km. The water is 2–4 m deep, with sludge-like organic sediments on the bottom. From spring through summer, the bottom layer of the inner harbor becomes a reducing environment, and generation of hydrogen sulfide has become a problem.\(^1\)\(^1\) Table 1 shows the properties of sediment collected from the bottom of the inner harbor. The high ignition loss indicates a high content of organic matter. During rain events, a large volume of untreated wastewater overflows from the combined sewage water treatment plant operated by Fukuyama City (rainwater and domestic sewage are collected in the same system). The main cause of deterioration of the bottom sediments in Fukuyama inner harbor is settling and accumulation of organic matter contained in this untreated wastewater.

2.2. Slag Construction

In August 2011, the first construction of steel-making slag was carried out at Test Site A (area: 432 m\(^2\); Fig. 1). Table 2 shows the chemical composition of the steel-making slag (Slag 1; produced at JFE Steel West Japan Works) used in the test. The slag was transported with a crane barge, and then set in place using a clamshell bucket attached to the crane. First, steel-making slag with a fine particle size of 5–10 mm was deposited to a thickness of 35 cm as the base material to prevent it from sinking into the soft bottom sediments during the experiments. Next, coarse (10–25 mm) steel-making slag was laid on the base material to a thickness of 35 cm to facilitate the exchange of seawater between the slag layer and the overlying water. During construction, a curtain-like frame was installed to prevent the dispersal of fine sediments to the surrounding environment when the slag was being applied.

In July of 2012, the second slag construction was carried out at Test Sites B and C (total area: 3 510 m\(^2\); Fig. 1). At Test Site B, Slag 1 (the same slag used at the first construction) was applied as both the base and top. At Test Site C, Slag 1 was used as the base material, while Slag 2 (see Table 2 for chemical composition) with a size of 30–50 mm was used on the top. In a previous study,\(^1\)\(^2\) the authors showed that Slag 2 plays a role as an adhesion base for seaweed and benthos in different waters. Therefore, Slag 2 was selected to investigate the possibility of growth of benthos on the slag. In both areas, the thicknesses of the bottom and top layer materials was 35 cm each (total thickness: 70 cm).

2.3. Monitoring

Gas, water quality, and benthos were investigated after the first slag construction (the first experiment; from August to June 2012) and after the second slag construction (the second experiment; from July 2012 onward). Figure 2 is a cross-sectional diagram showing the monitoring sites. As shown in Fig. 2(a), after the first construction, a\(_1\) (origin), a\(_2\) and a\(_3\) were set at the center, 5 m inner and outer in Test Site A, respectively. Monitoring at a\(_1\) was carried out during both the first and the second experiment period, and those

| Table 1. | Properties of silty sediment collected from Fukuyama inner harbor. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Water content | Sulfide (mg/g)  | COD (mg/g)      | T–N (mg/g)      | T–P (mg/g)      | Ig/loss (%)     |
| Ratio (%)      | 340             | 2.33            | 29.0            | 3.22            | 1.23            | 13.4            |

| Table 2. | Chemical composition of steel-making slags. |
|----------|---------------------------------------------|
| (mass%)  | T–Fe | SiO\(_2\) | CaO | Al\(_2\)O\(_3\) | MnO | MgO | TiO\(_2\) | P\(_2\)O\(_5\) |
| Slag 1   | 16.8 | 28.1 | 31.6 | 5.7 | 8.3 | 4.7 | 1.1 | 3.6 |
| Slag 2   | 23.2 | 14.2 | 47.3 | 3.5 | 3.0 | 6.9 | 0.6 | 1.3 |

Fig. 1. Location of the field test site and the enlarged map of slag construction area. (Online version in color.)

Fig. 2. Cross section diagrams of monitoring sites. (a) The first experiment (from August to June 2012), and (b) the second experiment (from July 2012 onward). (Online version in color.)
of a2 and a3 were done during the first experiment. Sites at 25 m, 50 m, and 100 m from the origin to the bay head and seaward from an area in which slag was not placed were set as control plots. During the second experiment period, in addition to a1, b (65 m seaward) in Test Site B and c (134 m seaward) in Test Site C were set as the monitoring sites for the slag experimental areas, and positions 100 m from the origin to the bay head and 244 m to the seaward side were set as control plots.

Monitoring was performed at 2, 8, 20 and 42 weeks after the first construction, and at 2, 12, 19, 30, 37, 41 and 46 weeks after the second construction.

2.4. Analytical Methods

2.4.1. Sediment Interstitial Water

Sampling of the interstitial water at the experimental sites was performed by connecting a Tygon® tube to an air stone that had been buried in advance at the time of slag construction at a depth of 5–10 cm from the slag surface. Samples were collected by a diver by using a syringe. In the control plots, 5–10 cm sediment core samples were collected with acrylic pipes having a diameter of 10 cm. The interstitial water was extracted by centrifugation.

The pH and oxidation-reduction potential (ORP) of water samples were measured with an IM-22P meter (DKK-Toa Corporation), while dissolved sulfide was measured using Kitagawa-type detection tubes (model 200SA, 200SB; Komyo Rikagaku Kogyo). The ORP value was converted to the Eh value \[\text{Eh} = \text{ORP} + 206 - 0.7(t - 25); t: \text{water temperature (°C)}\]. In the second experiment, the dissolved oxygen concentration was measured by Winkler’s method in addition to the aforementioned measurements.

2.4.2. Overlying Water

Overlying water at 5–10 cm above the surface of the steel-making slag or sediments was taken by divers and then collected from shipboard using a hand pump attached to a Tygon® tube in the second experiment. The pH, ORP, and concentrations of dissolved sulfide and dissolved oxygen were measured using the same methods as for the interstitial water of the sediments.

2.4.3. Vertical Profile of Water Quality

Vertical water quality profiles of the harbor water in and around the experimental areas were measured at an interval of 0.5 m in August and December of 2011 using a multi-parameter water quality analyzer (AAQ177; manufactured by JFE Advantech Co., Ltd.). In addition, water temperature, salinity, pH, dissolved oxygen concentration, and dissolved sulfide concentration were measured at various water depths at the same interval for the samples collected using a water sampler.

2.4.4. Gas Measurements

Gasses generated naturally from the sea bottom were collected by chambers placed on the bottom and quantified. In addition, divers collected samples from sea bottom sediments in December of 2012. After placing the samples in 300-ml-wide mouth bottles and shaking, the hydrogen sulfide concentration in the gas was measured using a gas detector tube (GX-2009; manufactured by Riken Keiki Co., Ltd.), and dimethyl disulfide and methyl mercaptan (CH3SH) were measured with gas detection tubes (model 53 and 71; Gastech Corporation).

2.4.5. Macrobenthos

Following the second experiment, quantitative analyses of macrobenthos were carried out on February 9, 2013 for Test Site C and control plot and on February 23, 2013 for Test Site A, B. Sediment samples with an area of 25 cm × 25 cm and a depth of 10 cm were collected by a diver, and the species number and individual numbers of the macrobenthos in the sediments were measured. At Test Site B and C, two samples were collected respectively, one was covered with fluffy sediments and the other was not covered with them.

3. Results

3.1. Interstitial Water

As shown in Fig. 3(a), the pH of the interstitial water from the control plots was slightly lower at the bay head (7.0–8.0) than on the seaward side (7.5–8.5). In the slag construction area, the pH was as high as 8.9 at Test Site A immediately after construction due to calcium ions eluted from the steelmaking slag, however decreased to around 7.1–8.0. At Test Sites B and C, the pH was around 7.9–8.4, with somewhat lower values at the bay head. A similar tendency was also observed in the control plots.

In the first experiment, the dissolved sulfide concentration ranged from the detection limit (0.5 mg/L) to 5 mg/L at Test Site A, while it ranged from 150 to 350 mg/L in the control plots (Fig. 3(b)). The situation was the same in the second
experiment. Specifically, the dissolved sulfide concentrations were remarkably low, ranging from the detection limit to 20 mg/L at Test Sites B and C, while it was relatively high (60–400 mg/L) in the control plots.

The Eh of the interstitial water is shown in Fig. 3(c). In the first experiment, the levels in the control plots were low (approximately −200 mV), regardless of the measurement dates. However, in the slag construction area, samples were higher than in the control plots, ranging from −20 to +100 mV. Although the decrease was observed from after 2 weeks to after 8 weeks, Eh increased in winter (December), showing a seasonal change. The same seasonal variation was also observed in the second experiment, ranging from −20 to +100 mV in the slag construction area. The Eh was also approximately the same level at Test Sites B and C in the second experiment.

The dissolved oxygen concentrations of the interstitial water after the second experiment are shown in Fig. 3(d). From autumn through winter, the dissolved oxygen concentration of the interstitial water was higher in the slag construction area than in the control plots.

3.2. Overlying Water

Figure 4 shows the dissolved sulfide concentration, Eh, and dissolved oxygen concentration of the overlying water in the slag construction area and the control plots. No dissolved sulfide was detected in the slag construction area or the control plots, regardless of the time of year. Eh and dissolved oxygen were low in summer and high in winter, but virtually no differences were observed between slag construction areas and control plots.

3.3. Vertical Profile of Water Quality

Figures 5 and 6 show the water quality profiles for August 2011 and December 2011. There were no clear differences in the vertical profiles of water quality between the slag construction area and the control plots on either sample date. In August 2011, a large change occurred at approximately 2 m, indicating that a layer of discontinuity had occurred. The dissolved oxygen concentration at ≥2 m was clearly anaerobic. Conversely, the water quality was similar...
from the surface to the bottom in December 2011, with a high dissolved oxygen concentration even in the bottom layer.

3.4. Gas Generated in the Bottom Sediments

3.4.1. Volume of Generated Gas

The volumes of gas generated in the bottom sediments are shown in Fig. 7. Although the volume varied depending on the time of year, it ranged from 0 to 0.03 cm³/cm²/h in the slag construction area, while it was 0–0.23 cm³/cm²/h in the control plots.

3.4.2. Composition of Gas

The gas composition after shaking the sediments sampled in December 2012 is shown in Fig. 8. Hydrogen sulfide, dimethyl disulfide and methyl mercaptan were detected. While hydrogen sulfide gas was below the detection limit (<1 ppm) in the bay head and 1 200 ppm on the seaward side, dimethyl disulfide and methyl mercaptan were not detected in the treatment areas, while they were present at 70 ppm and 10 ppm, respectively, in the control area. These results showed that other malodorous components in the bottom sediments in addition to hydrogen sulfide were remarkably suppressed.

3.5. Macrobenthos

Adhesion of macrobenthos was observed from winter through spring on the surface of slag. Figure 9 shows the species number, individual numbers, and wet weight of macrobenthos in February 2013. In the slag construction area, 3–6 species were observed, including annelids and mollusks. Overall, there were 500–1 400 individuals with a wet weight of 5–23 g per 0.1 m². In particular, different kinds of macrobenthos such as Ciona savignyi and spinonids were observed inhabiting at Test Site C, which was the site located most seaward. In contrast, 1 or 2 species of annelida were observed in the control plots, with 20–150 individuals and a wet weight of 0.5–1 g per 0.1 m². Figure 10 shows underwater photographs of Test Site C and the seaward control plot. As shown in the photograph of Test Site C, Ciona savignyi and Pseudopolydora paucibranchiata adhered to the surface of the slag in this area.

4. Discussion

4.1. Detoxification of Dissolved Sulfide in Field Bottom Sediments by Steel-making Slag

Hydrogen sulfide is formed by the reduction of sulfate ions ($SO_4^{2-}$) when sulfate-reducing bacteria decompose organic matter in sediments under anaerobic conditions as shown in Eq. (1). 13)

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

Hydrogen sulfide mainly exists in water mainly as hydrogen sulfide ions ($HS^-$), some of which are eluted from the bottom sediments into overlying water.

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**Fig. 7.** Volume of gas generated from the bottom sediments (see Figs. 4–5 regarding the sampling device). ○: control (bay head, 100 m from a1). ▲: a1, ■: b, ●: c, △: control (sea side 100 m from a1). ◎: control (seaside, 244 m from a1). (Online version in color.)

**Fig. 8.** Hydrogen sulfide, methyl mercaptan and dimethyl disulfide concentration in the bottle after shaking (December 2012). (Online version in color.)

**Fig. 9.** Species number, individual number and wet weight of macro benthos observed in and on the sediments. Samples were collected from a1 and the control plots. They were also collected from Test Site B and C at which both covered with fluffy sediments and without them. Sampling was carried out on February 9, 2013 for c and control plots, and on February 23, 2013 for the other plots.

**Fig. 10.** Macrobenthos observed at c without fluffy sediment and at Control plot in February 2013. (Online version in color.)
In previous laboratory experiments conducted using sediments collected from Fukuyama inner harbor,4) the authors showed that elution of dissolved sulfide and generation of gasses in the overlying water and interstitial water could be suppressed by placing steel-making slag on the bottom sediments (capping) and then mixing the slag in the sediments. In the present study, field tests conducted based on the results of laboratory tests showed that the effects of suppressing dissolved sulfide in the slag interstitial water and reducing the volume of gas generation continued for at least two years (Fig. 3). A reduction in the volume of hydrogen sulfide gas was also observed.

Hayashi et al. conducted EPMA element mapping of the slag surface after reacting steel-making slag with an aqueous solution of sodium sulfide and reported good agreement of the distributions of sulfur (S) and iron (Fe) at the slag surface.8) Non-reflective X-ray diffraction analysis and synchrotron radiation analysis of the reaction product implied that formation of iron sulfide and elemental sulfur had occurred. It is assumed that these changes occurred via the reactions expressed in Eqs. (2) and (3).8)

\[
\text{HS}^- + \text{Fe}^{3+} \rightarrow \text{FeS} + \text{H}^+ \quad \text{(2)}
\]

\[
\text{HS}^- + 2\text{Fe}^{3+} \rightarrow \text{S}^0 + 2\text{Fe}^{2+} + \text{H}^+ \quad \text{(3)}
\]

In the present study, there is also a possibility that Fe was eluted from the slag and contributed to the suppression of sulfide in sediments by forming iron sulfide and elemental sulfur via the reactions shown in Eqs. (2) and (3). In the previous paper, we showed good correspondence of Fe and S on the surface of steelmaking slag immersed in the Fukuyama inner harbor sediments for four months by the scanning electron microscopy.3) It suggests that FeS was formed on the surface of the steelmaking slag.

In the overlying water, no differences in dissolved sulfide concentrations and other parameters were detected between the slag construction area and the control plots, indicating that advective diffusion caused by tidal currents may have had a large effect. To verify this, cylindrical chamber devices (vinyl chloride, diameter 150 mm × height 300 mm) as shown in Fig. 11(a) were placed at each monitoring site in November of 2012 to separate the sediments and bottom water, and the concentration of dissolved sulfide eluted from the sediments was measured with detection tubes after 12 days (December 2012) and 86 days (February 2013). The results of these measurements are shown in Fig. 11(b). In the control plots, a dissolved sulfide concentration of 50 mg/L was observed at the bay head, and a concentration of 6–45 mg/L was observed on the seaward side. In contrast, the concentration in the slag construction area was low, ranging from the detection limit (< 0.5) to 5 mg/L. Based on these results, the effects of suppressing elution of dissolved sulfide from the bottom sediments into the overlying water observed in the laboratory experiments5) were confirmed.

### 4.2. Recovery of Dissolved Oxygen Concentration from Autumn through Winter

In the present study, recovery of dissolved oxygen from autumn through winter was observed after the decrease (oxygen deficiency) from spring through summer as illustrated in Figs. 4(d) and 5. It is well known that oxygen deficiency occurs in the bottom layer at the bay head of enclosed bodies of water such as Tokyo Bay and Osaka Bay during summer because of the formation of a thermocline, while the oxygen levels of the bottom waters increase in winter as a result of vertical mixing.14–16) It is assumed that a similar annual change is also occurring at Fukuyama inner harbor.

However, even though the dissolved oxygen concentration of the overlying water increased, the dissolved oxygen concentration of the interstitial water in the sediments in the control plots did not increase from autumn through winter. This was likely because a large amount of dissolved sulfide exists in the interstitial water in the sediments of control plots, which consumes the dissolved oxygen at the bottom layer as shown in Eq. (4).

\[
\text{2H}_2\text{S} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{S} \quad \text{(4)}
\]

Conversely, the dissolved oxygen concentration in the interstitial water in the sediments increased in the slag construction area. Because the dissolved sulfide concentration is low in the slag construction area, this increase in dissolved oxygen concentration was attributed to decreased consumption of dissolved oxygen by hydrogen sulfide as shown in Eq. (4). The dissolved oxygen concentration in the overlying water increased from autumn through winter. However, this could have been due to high water exchange between the slag interstitial water and the overlying water, which was possible because of the large particle size of the slag used for the upper layer material.

### 4.3. Adhesion of Macrobenthos from Winter through Spring

During winter, a large number of macrobenthos inhabited Test Site C, which was the site closest to the sea. This seems to be attributed to the formation of a favorable environment, particularly in the slag construction area, because of the increased dissolved oxygen concentration of the interstitial water (see Section 4.2). This type of environment may be favorable for macrobenthos such as *Ciona savignyi*, which
usually live attached to stable bases such as shoreline rocks. On the other hand, *Ciona savignyi* was not observed in Test Site B, this was likely because the grain size of Slag 1 is too small to form a stable base.

The *Ciona savignyi* observed living in Test Site C are known to be a type of filter feeder that remove suspended matter by filtering sea water. It may be possible to increase the suspended matter purification capacity by expanding the area in which suspension feeders such as *Ciona savignyi* reside by increasing the area of slag construction and reducing the sewage input load.

4.4. Applicability of Steel-making Slag for Reduction of Hydrogen Sulfide in Silty Sediments

The present study and the results of a previous report demonstrated that steel-making slag can improve organically enriched sediments with no adverse environmental effects associated with extraction of natural materials. The remediation of sulfide containing sediments with steel-making slag is based on chemical reactions such as adsorption and oxidation of hydrogen sulfide, which cannot be performed with natural stones.

Overall, these results suggest that steel-making slag is an effective material for improvement of bottom sediments in inner harbors, inlets and in mariculture areas where feed and other organic materials accumulate. Steel-making slag also has the potential for use as a refilling material for dredged pits present in Tokyo Bay and other bays, in which oxygen-deficient water masses are formed and may cause blue tides.

5. Conclusion

Steel-making slags were used to prevent generation of hydrogen sulfide from organically rich sediments. The treatment area consisted of 430 m² in August 2011 and 3 510 m² in July 2012. After construction, the water and sediment quality along with gasses generated from the sediments were monitored. The following results were obtained over a period of approximately 2 years.

(1) Dissolved sulfide in the interstitial water of sediments in the slag treatment area was reduced remarkably relative to that in the control plots. The oxidation-reduction potential (ORP) and dissolved oxygen were also improved, and the effects continued for at least 2 years. This could have been due to the formation of iron sulfide and oxidation to elemental sulfur by reactions between iron ions eluted from the slag and dissolved sulfide in the area.

(2) A decrease in the total volume of gas generated from the sediments was observed in the slag construction area. The concentration of hydrogen sulfide gas also decreased.

(3) No differences in the quality of the overlying water or that of the upper water layer were observed between the slag construction area and the control plots, indicating that water exchange due to advection and diffusion caused by tidal currents are prevailing.

(4) From autumn through winter, recovery in of dissolved oxygen in the sediment interstitial water was observed in the slag construction area, whereas no such phenomenon was observed in the control plots. This may have been due to a decrease in oxygen consumption by dissolved sulfide. The use of coarse slag in the upper layer may have facilitated the exchange of seawater between the interstitial and overlying water.

(5) Adhesion of macrobenthos was observed from winter through spring on the surface of slag. In particular, different kinds of macrobenthos such as *Ciona savignyi* and spinonids were observed inhabiting Test Site C, which was the site located most seaward. In addition to the recovery of dissolved oxygen in the bottom layer, decreasing thickness of the deposited fluffy sediments, which led to partial exposure of the slag surface, may have provided a habitat for *Ciona savignyi*.

Taken together, these results indicate that capping with steel-making slag is an effective technique for improvement of organically enriched bottom sediments containing hydrogen sulfide because it leads to induction of chemical reactions between Fe and sulfide occurring in sediments that do not occur under natural conditions.

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