

Control of Sulfide Release from Bottom Sediments at Borrow Pits Using Steelmaking Slag

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ABSTRACT

There are many borrow pits caused by sand mining at the bottom of the coastal sea in Japan. Borrow pits have been identified as a source of oxygen-deficient water with hydrogen sulfide. It has become increasingly important to restore borrow pits to improve the marine environment. However, large quantities of sand materials are needed to restore borrow pits. Recently, dredged materials generated by sea route maintenance have been adopted instead of sand materials. However, one problem of dredged materials is that they can be weak ground materials. Therefore, slag-mixed material made from the dredged material and steelmaking slag has been proposed. In this study, control of hydrogen sulfide release resulting from changing the hardness of the slag-mixed materials has been examined. Hydrogen sulfide release strongly depends on the hardness of the slag-mixed material. Microbial analysis indicated fewer living bacteria and the relative abundance of sulfate-reducing bacteria in the slag-mixed material compared with the dredged material. The solidification of the dredged material using steelmaking slag decreased not only hydrogen sulfide release but also dissolved iron and manganese release. It is considered that controlling the hardness of the dredged material mixed with steelmaking slag provides an effective means of sulfide release control.

Keywords: dredged material, hydrogen sulfide, steelmaking slag

INTRODUCTION

There are many borrow pits caused by sand mining at the bottom of the coastal sea in Japan. For example, the Makuhari Area of Tokyo Bay has approximately 10,000 m³ of borrow pits. In summer, borrow pits easily accumulate hydrogen sulfide and become a source of oxygen-deficient water that kills marine organisms. In Japan, the phenomenon is called blue tide (Suzuki, 2001; Suzuki *et al.*, 2003; Nakamura, 2006). Because of the increasing prevalence of blue tides, public awareness of the importance of restoring borrow pits to improve the marine environment has increased. However, the large amount of sand material needed to restore borrow pits is a problem. For this reason, rather than sand materials, dredged materials generated by sea route maintenance have been adopted to restore borrow pits in Mikawa Bay. It has been reported that dissolved oxygen concentration has been recovered by restoring borrow pits using dredged materials (Ishida and Suzuki, 2006). However, problems with the dredged materials, such as weak ground, easy dispersion, and a high ratio of organic compounds are encountered. Slag-mixed material made from dredged material and steelmaking slag has been proposed to solve such problems (Nakagawa and Kiso, 2011). Steelmaking slag is generated in the converter steel making process or the electric steel making process. The particular steelmaking slag proposed here is converter slag. The mechanism to improve the hardness of dredged materials using steelmaking slag is as follows: SiO₂ contained in the dredged materials and CaO contained in the steelmaking slag produce calcium

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silicate hydrate, $\text{CaO-SiO}_2\text{-H}_2\text{O}$ (C-S-H). This is called the pozzolanic reaction. The slag-mixed materials can be expected to not only improve hardness but also control phosphorous or hydrogen sulfide that is released from bottom sediments at borrow pits (Miki *et al.*, 2009, 2011; Nakagawa and Kiso, 2011). However, there is no definitive explanation for the mechanism by which hydrogen sulfide release is controlled using the steelmaking slag mixture. For example, the inhibition of sulfate-reducing bacteria (SRB) was considered to be due to the higher pH caused by alkaline components released from the steelmaking slag. Also, dissolved iron released from the steelmaking slag was considered to react with hydrogen sulfide released from bottom sediments, producing iron sulfide (FeS) and decreasing dissolved hydrogen sulfide concentration (Nakagawa and Kiso, 2011).

In this paper, the relationship between hydrogen sulfide release and the hardness of the slag-mixed material was examined by changing the hardness relative to the amount of steelmaking slag. And, from a microbial analysis of the solidified slag-mixed material and the dredged material, the control mechanism for hydrogen sulfide release was examined. These test results have clarified that the solidified slag-mixed material decreases the number of living bacteria, the comparative number of SRB, and hydrogen sulfide release from the dredged material.

MATERIALS AND METHODS

Sulfide release control test using solidified slag-mixed material (RUN1, RUN2)

Dredged materials were gathered from Tokyo Bay (Haneda area) and Mikawa Bay and were used for RUN1 and RUN2, respectively. Table 1 gives the characteristics of the dredged material from Tokyo Bay, the dredged material from Mikawa Bay, and steelmaking slag. Table 2 shows the experimental conditions of RUN1. Steelmaking slag (particle size: 0 – 25 mm) was added to the dredged material from Tokyo Bay from 0 wt% to 38 wt%. A total of 6 samples per dredged material (T0 – T5) were used for RUN1. Table 3 shows the experimental conditions of RUN2. The dredged material from Mikawa Bay was not easily solidified by 50 wt% addition of steelmaking slag. Therefore, granulated blast furnace slag (GBF slag) was additionally added to the dredged material to promote solidification. Granulated blast furnace slag is well known for promoting self-solidification under alkali-stimulant conditions and is used for cement material. A total of 5 samples per dredged material (M0 – M4) were used for RUN2. The dredged materials or the slag-mixed materials were added to 1 L glass bottles. The bottles were filled with 900 mL of artificial seawater (24.55 g NaCl; 0.695 g KCl; 1.535 g $\text{CaCl}_2\cdot 2\text{H}_2\text{O}$; 11.115 g $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$; 4.094 g Na_2SO_4 ; 0.201 g NaHCO_3 ; 0.10 g KBr; 0.027 g H_3BO_3 ; 0.003 g NaF; 0.0425 g $\text{SrCl}_2\cdot 6\text{H}_2\text{O}$; 1 L distilled water); dissolved oxygen was eliminated using nitrogen bubbling. The samples were incubated statically for 30 days at room temperature under dark/anoxic conditions. To promote the sulfide generation using SRB, 25 mg of glucose was mixed into 50 g of the dredged materials. Filtered seawater was collected using a syringe with a membrane filter of 0.45 μm pore size after 3, 10, and 30 days. Dissolved sulfide concentrations in the seawater were analyzed. The indentation hardness of the dredged materials and the slag-mixed materials were measured after 3, 10, and 30 days.

Table 1 - Characteristics of steelmaking slag and the dredged material from Tokyo Bay, and Mikawa Bay (RUN1, RUN2).

		Material from Tokyo Bay	Material from Mikawa Bay	Steelmaking slag
Bulk density	[g/cm ³]	1.48	1.31	2.95
Water content	[%]	36.1	68.3	11.4
COD _{Mn}	[mg/(g-dry material)]	5.4	19.7	5.5
Sulfide	[mg/(g-dry material)]	0.19	0.40	0.07

Table 2 - Experimental conditions using the dredged material from Tokyo Bay, and Mikawa Bay (RUN1, RUN2).

Sample	T0	T1	T2	T3	T4	T5
Dredged material [g-wet material]	50	50	50	50	50	50
Steelmaking slag [g-wet material]	0	2	5	10	25	30
Glucose [mg]	25	25	25	25	25	25

Table 3 - Experimental conditions using the dredged material from Mikawa Bay (RUN2).

Sample	M0	M1	M2	M3	M4
Dredged material [g-wet material]	50	50	50	50	50
Steelmaking slag [g-wet material]	0	50	50	50	50
GBF slag [g-wet material]	0	0	0.5	1	5
Glucose [mg]	25	25	25	25	25

Control mechanism for sulfide release using solidified slag-mixed material (RUN3)

Dredged material gathered from Tokyo Bay was used for RUN3. Table 4 shows the characteristics of the dredged material from Tokyo Bay and the steelmaking slag used in RUN3. To promote the sulfide generation using SRB, glucose was mixed in the dredged materials. As shown in Table 5, the dredged material or the slag-mixed material was added to 1 L glass bottles and the bottles were filled with the same artificial seawater. Dissolved oxygen was eliminated using nitrogen bubbling. Four samples were prepared in the same manner for each experimental condition. Filtered seawater was collected using a syringe with a membrane filter of 0.45 µm pore size after 5, 10, 40, and 60 days. The sulfide, Fe, and Mn concentrations of the seawater were analyzed. Microbial analysis was done for the dredged material and the slag-mixed materials after 60 days.

Table 4 - Characteristics of the dredged material from Tokyo Bay and steelmaking slag (RUN3).

		Material from Tokyo Bay	Steelmaking slag
Bulk density	[g/cm ³]	1.34	3.06
Water content	[%]	57.6	9.46
COD _{Mn}	[mg/(g-dry material)]	12.0	2.4
Sulfide	[mg/(g-dry material)]	0.26	0.17

Table 5 - Experimental conditions using the dredged material from Tokyo Bay (RUN3).

	Slag-mixed material	Dredged material
Dredged material [g-wet material]	50	100
Steelmaking slag [g-wet material]	50	0
Glucose [mg]	25	50

ANALYTICAL METHODS

Dredged material, slag-mixed material, steelmaking slag, and seawater analysis

Water, COD, and sulfide content were analyzed according to the Bottom Sediments Survey Manual (Water Quality Bureau of the Environment Agency, 1996). Indentation hardness was measured by Yamanaka soil hardness tester (Fujiwara Scientific Company).

Wet density was measured according to JGS 0191 (Japanese Geotechnical Society, 2008). Seawater quality was analyzed by a method adopted from JISK 0102 (Japanese Standards Association, 2008). Samples were filtered through a membrane filter (0.45 µm pore size). The dissolved sulfide of the sample was immediately fixed as ZnS with zinc acetate. Zinc sulfide was remelted and the dissolved sulfide was measured using an iodometric titration flow method. Dissolved Fe and Mn were analyzed using ICP-optical emission spectrometry (ICPE-9000, Shimadzu Corp., Japan).

Microbial analysis

Intracellular adenosine triphosphate (ATP) in microbial cells

The bacterial number in the dredged material or the slag-mixed material was estimated by measuring the intracellular ATP in the microbial cells using a Microbial ATP Kit HS (BioThema AB, Sweden). The light emission was measured before and after the addition of a known amount of standard ATP. The bacteria number was estimated under the assumption: 2×10^{-18} mol ATP/cell.

Relative quantification of SRB in dredged material using real-time polymerase chain reaction (PCR)

The dredged materials or the slag-mixed materials, collected from the glass bottles, were mechanically destructed by FastPrep 24 instrument (Funakoshi Co., Japan). Total nucleic acids were extracted from 0.5 g (wet material) of the destructed samples using

the ISOIL for Beads Beating (Nippon Gene Co. Ltd., Japan). Average DNA amount recovered from the samples was 200 ng/g. After the final ethanol precipitation, the nucleic acids were resuspended in 100 µL of Tris-EDTA (TE) buffer (10 mM Tris-HCl, 1 mM EDTA [pH 8.0]). One microliter of the DNA extract was diluted tenfold with TE and used for real-time PCR.

The relative abundance of SRB in the slag-mixed material or the dredged material was performed by the comparative threshold cycle (Ct) method using real-time PCR with a SYBR Green I assay. Fold change was used to compare the gene expression in two different samples (slag-mixed material and dredged material); each sample was related to an internal control gene (Schmittgen and Livak, 2008).

$$\Delta Ct = Ct_{\text{gene of interest}} - Ct_{\text{internal control}} \quad (1)$$

$$\Delta\Delta Ct = [(Ct_{\text{gene of interest}} - Ct_{\text{internal control}})_{\text{sample A}} - (Ct_{\text{gene of interest}} - Ct_{\text{internal control}})_{\text{sample B}}] \quad (2)$$

$$\text{Fold change due to steelmaking slag mixture} = 2^{-\Delta\Delta Ct} \quad (3)$$

The gene of interest is SRB and the internal control is a gene of the bacteria. Sample A is slag-mixed material and Sample B is dredged material (calibration material). Table 6 shows PCR primers for the amplification of each gene. EUB341F-UNIV907Rdeg and DELTA495aF-UNIV907Rdeg were used for the determination of bacteria and SRB, respectively (Imai *et al.*, 2004).

Table 6 - PCR primers for the amplification of gene.

Primer	Sequence (5' – 3')
UNIV907.degR	CCG TCA ATT CCT TTR ^{a)} AGT TT
EUB341F	CCT ACG GGA GGC AGC AG
DELTA495aF	AGT TAG CCG GTG CTT CCT

a) R: A or G

RESULTS AND DISCUSSION

Sulfide release control by solidification using steelmaking slag (RUN1, RUN2)

Figure 1 shows the time course changes of the hardness of the slag-mixed material with different ratios of slag to dredged material. For the dredged material from Tokyo Bay, at steelmaking slag amounts from 17 to 38 mass%, the hardness of the slag-mixed materials reached over 500 kPa after 5 days (T3 – T5). Digging into the material with fingers became difficult when the hardness increased over 500 kPa. In the case of the dredged material from Mikawa Bay, the hardness of the slag-mixed material after 30 days did not reach 200 kPa even at the slag addition ratio of 50 mass% (M1). However, the addition of GBF slag promoted the hardness of the slag-mixed materials (M2 – M4). The hardness of M3 and M4 samples reached over 500 kPa after 30 days. The solidification of the dredged material from Mikawa Bay was more difficult than that of the dredged material from Tokyo Bay. Water content and the organic matter in the dredged materials are considered to be the inhibition factors for solidification using steelmaking slag. Organic compounds, such as sodium gluconate, are widely known inhibitors because Ca ion complexes suppress the solidification reaction.

Figure 2 shows the relationship between the hardness of the slag-mixed materials after 10 days and the dissolved sulfide concentrations. In the case of the dredged material, dissolved sulfide release easily occurred with time. And, when the hardness of the slag-mixed material was rather small, dissolved sulfide release control was difficult. The dissolved sulfide concentration in seawater tended to decrease when the hardness of the slag-mixed materials increased. When the hardness of the slag-mixed materials reached over 500 kPa, the stable sulfide release control effect was obtained. It seemed that achieving dissolved sulfide release control by varying the amount of steelmaking slag in the mixture was rather difficult. In the case of slag-mixed material made from the dredged material from Tokyo Bay, a 10% mixture of steelmaking slag sufficiently restrained the sulfide release (T3). However, in the case of slag-mixed material made from the dredged material from Mikawa Bay, even 50 wt% of steelmaking slag could not restrain the release of dissolved sulfide (M1). And, for example, pH of the seawater of M1 was 9.2 and pH of the seawater of T2 was 8.6. The results suggested that higher pH did not limit the dissolved sulfide release.

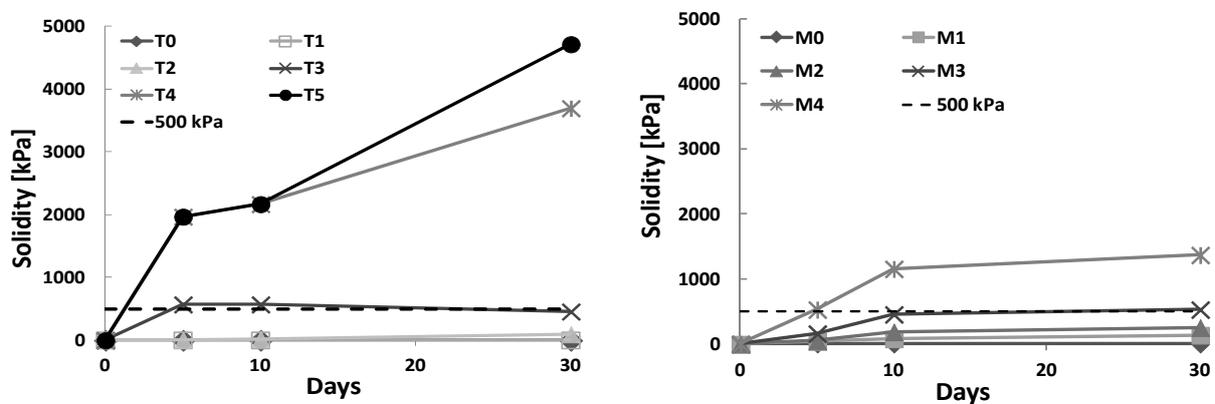


Fig. 1 - Time course changes of the hardness of the dredged material and the slag-mixed material with different slag addition ratios (Left: Tokyo Bay; Right: Mikawa Bay).

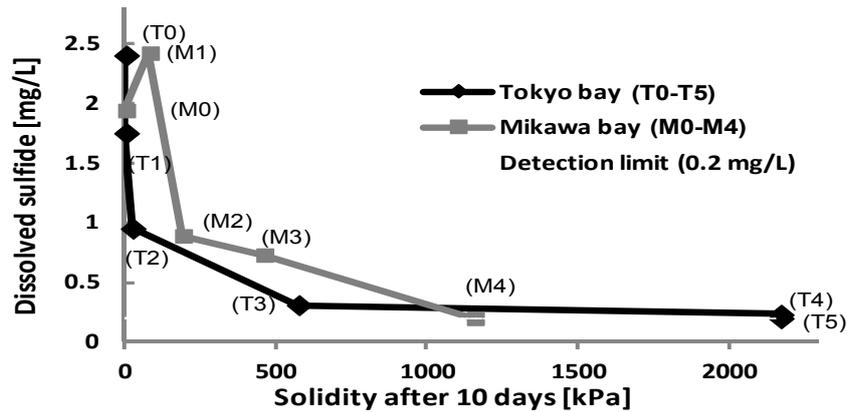


Fig. 2 - Relationship between the hardness of the slag-mixed material after 10 days and the dissolved sulfide concentrations.

These experiments showed that the dissolved sulfide release was limited by the hardness of the slag-mixed material rather than the amount of steelmaking slag in the mixture. It was estimated that the solidification of the dredged material mixed with steelmaking slag inhibited the sulfate-reducing reaction.

Control mechanism for sulfide release using steelmaking slag (RUN3)

Living bacterial number

The bacterial number of the slag-mixed material was 1.22×10^6 cell/(g-dry material), which was only 2.6 mass% of the bacterial number of the dredged material, 4.59×10^7 cell/(g-dry material). The results show that the bacterial number of the slag-mixed material decreased beyond steelmaking mixture rate.

Relative abundance of SBR by comparative Ct method using real-time PCR

Figure 3 shows PCR amplifications of bacteria and SRB in the slag-mixed material and the dredged material from Tokyo Bay. Table 7 shows the relative quantity using the comparative Ct method. Fluorescence intensity (FI) was set at 0.2 at the start of exponential growth, which determined Ct. Equations (1) and (2) gave ΔCt and $\Delta\Delta Ct$, respectively, and $2^{-\Delta\Delta Ct}$ was determined. When dredged material from Tokyo Bay was used as the calibrator, fold change due to the slag mixture ($2^{-\Delta\Delta Ct}$) became 0.334. Furthermore, when ATP was used to estimate the total bacterial number, the SRB number of the slag-mixed material was estimated from $2^{-\Delta\Delta Ct}$. As a result, the SRB number in the slag-mixed material decreased to 0.9% or less ($0.026 \times 0.334 = 0.00868$) compared with that of the dredged material from Tokyo Bay.

From these results, it can be seen that the relative abundance of SRB was reduced by the solidification using steelmaking slag, which would hinder the hydrogen sulfide release. In addition, the solidification of the dredged materials may hinder the mass transfer inside the solidified materials. But, the verification of the containment effect is quite difficult because it is hard to get pore water inside the solidified materials.

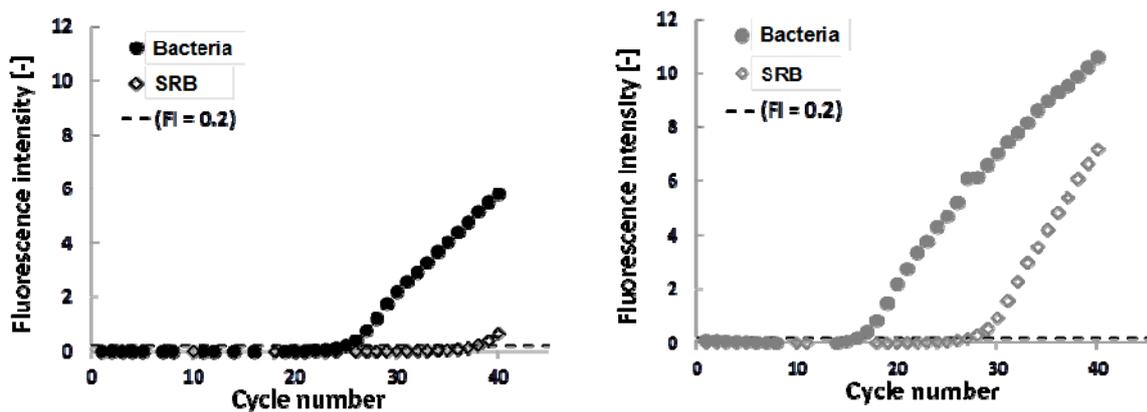


Fig. 3 - PCR amplifications of bacteria and SRB in the slag-mixed material and the dredged material (Left: slag-mixed material; Right: dredged material).

Table 7 - Relative quantification using comparative Ct Method.

	Ct (Bacteria)	Ct (SRB)	Δ Ct	$\Delta\Delta$ Ct	Relative Quantity
Slag-mixed material	24.8	37.4	12.7	1.58	0.334
Dredged material	16.0	27.1	11.1	0.00	1

Dissolved sulfide, manganese, and iron

The dissolved sulfide concentration in the seawater of the dredged material sample reached over 35 mg/L after 60 days. Dissolved sulfide concentration in the seawater of the slag-mixed material sample was under 3 mg/L after 60 days. These experimental results can be explained by the results for the SRB numbers previously mentioned. These results proved that the strong inhibition of the sulfate reduction reaction using SRB occurred relative to the solidification of the steelmaking slag mixture. The dredged material from Tokyo Bay contained manganese dioxide (MnO_2) and ferric hydroxide ($\text{Fe}(\text{OH})_3$). Such manganese and iron compounds are easily reduced by microorganisms, manganese-reducing bacteria, or iron-reducing bacteria under anaerobic conditions with plenty of organic matter. Manganese and iron reduction are followed by sulfuric acid reduction. It was estimated that, like the sulfate reduction reaction, manganese and iron reduction reactions using microorganisms are inhibited by the degree of solidification. Time course changes of dissolved manganese and iron concentrations are shown in Fig. 4. This indicated that both manganese and iron reduction easily occurred in the dredged material from Tokyo Bay. Dissolved iron was detected only during the initial experimental period and then the concentration decreased, which meant that iron sulfide (FeS) was gradually formed by the reaction between the dissolved iron and sulfide. Dissolved manganese was continuously detected in the seawater during all experimental periods, which suggested that the solubility of manganese sulfide (MnS) was greater than that of iron sulfide (FeS).

On the other hand, it was observed that neither dissolved iron nor manganese were detected in the seawater of the slag-mixed material, which strongly suggested that both

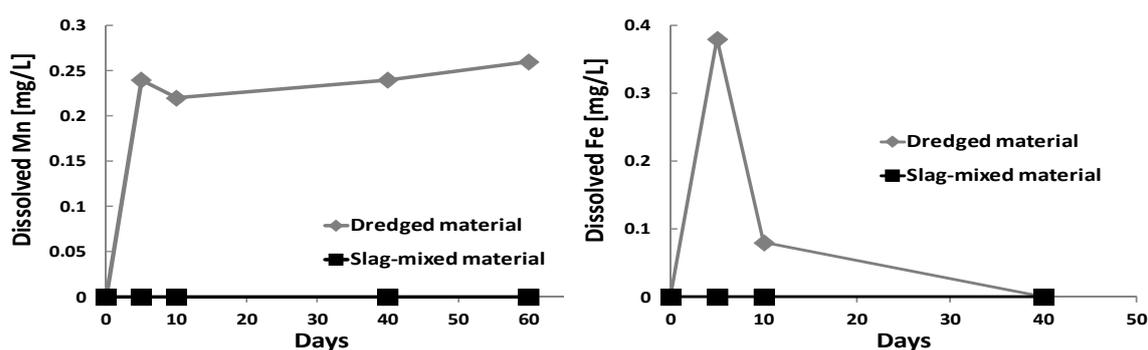


Fig. 4 - Time course changes of dissolved manganese and iron concentration in seawater. (Left: Mn; Right: Fe).

manganese and iron reduction by microorganisms were inhibited by solidification. From these experimental results, there is a strong possibility that the solidification of the dredged material using steelmaking slag inhibited not only the sulfate-reduction reaction but also the iron and manganese reduction reactions.

CONCLUSIONS

The solidification of the dredged material using steelmaking slag proved to reduce the dissolved sulfide release in the seawater from the dredged material. The dissolved sulfide release is limited by the hardness of slag-mixed material. However, the dissolved sulfide release is not necessarily limited by the amount of steelmaking slag in the slag-mixed material. Microbial analysis of the solidified slag-mixed material proved the decrease of the living bacteria and the relative abundance of SRB compared with the dredged material. The solidification of the dredged material mixed with steelmaking slag reduced the dissolved iron and manganese concentrations. There was a strong possibility that the solidification of the dredged material mixed with steelmaking slag could not only inhibit the sulfate-reduction reaction but also the iron and manganese reduction reactions. We conclude that the hardness control of the dredged materials using steelmaking slag provides an effective means of minimizing sulfide release from bottom sediments at borrow pits.

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