Mechanism of Suppression of Sulfide Ion in Seawater Using Steelmaking Slag

Akio HAYASHI,1,2)* Satoshi ASAOKA,3) Tetsuya WATANABE,1) Ryoko KANEKO,1) Katunori TAKAHASHI,2) Yasuhiro MIYATA,2) Kyunghoi KIM,4) Tamiji YAMAMOTO,2) Ryo INOUE5) and Tatsuro ARIYAMA5)

1) JFE Mineral Corporation, 1, Niihama-cho, Chuo-ku, Chiba, 260-0826 Japan. 2) JFE steel Corporation, 1, Kawasaki-cho, Chuo-ku, Chiba, 260-0835 Japan. 3) Formerly Environmental Research and Management Center, Hiroshima University. Now at Research Center for Inland Seas, Kobe University, 1-1, Rokkoudai-Chou, Nada-ku, Kobe, 657-8501 Japan. 4) Graduate School of Biosphere Science, Hiroshima University, 4-4-1, Kagamiyama, Higashihiroshima, 739-0046 Japan. 5) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 1-1-2, Katahira, Aoba-ku, Sendai, 980-8577 Japan.

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In Japan, 15 million tons of steelmaking slag is produced annually as a by-product of the steelmaking process. It is known that steelmaking slag has specific properties to decrease hydrogen sulfide in seawater. To date, however, the specific mechanism is still unknown. This is the first report that explains the process of the slag reducing the hydrogen sulfide level.

We added slag to the artificial seawater containing sulfide ion and obtained fine particles. We analyzed the reaction products with X-ray absorption fine structure (XAFS) and scanning electron microscopy-energy dispersive X-ray detector (SEM-EDX) and confirmed corresponding peaks of FeS, FeS₂, sulfur and sulfate.

We also measured the oxidation-reduction potential (ORP) and found that a shift to oxidizing atmosphere was promoted by adding slag, which oxidized sulfide ion to sulfuric acid ion.

These data suggested that hydrogen sulfide level in seawater is reduced not only by the reaction of sulfide with iron contained in steelmaking slag but also by oxidation of sulfide in seawater with steelmaking slag. These results imply that effective utilization of steelmaking slag in coastal areas has a capability to improve the surrounding marine environment.

KEY WORDS: steelmaking slag; hydrogen sulfide; sediment; seawater environment; XAFS.

1. Introduction

The steel manufacturing process produces a large number of by-products, among which the Japanese steel industry generates 40 million tons of iron and steelmaking slag each year. Although reuse of slag has approached 100% for many years, technical development is continuing with the aim of realizing effective utilization with higher added value. The ironmaking process generates 25 million tons/year of blast furnace slag, of which more than 60% is used in a high value-added application as Portland blast furnace slag cement, taking advantage of the hydraulic property of blast furnace slag.1) The steelmaking process generates 15 million tons/year of steelmaking slag, with road construction and civil works accounting for 60% of reuse. While blast furnace slag is used in a high value-added application that utilizes its special properties, high value-added applications that actively use the physical properties and composition of steelmaking slag have not been adequately developed.1) Because steelmaking slag usually has an iron content of close to 20%, recent research on higher added value-added uses has focused on its Fe content, and improvement measures against coastal denudation using Fe ions eluted from steelmaking slag2) and bottom sediment improvement measures for an enclosed coastal sea3,4) have been reported.

At dredging sites in enclosed waters and sea areas with accumulated bottom sludge, the reduced oxygen content associated with higher water temperatures in summer, stagnant water masses, and oxygen deficiency due to decomposition of organic matter deposited in the bottom sediments create an environment which is suitable for propagation of sulfide-reducing bacteria, resulting in generation of hydrogen sulfide.5) This causes problems such as deterioration of the biological environment, foul smells, and the like. As one example, in Tokyo Bay, many sea-bottom depressions exist at former dredging sites, the dissolved oxygen concentration decreases dramatically in summer, and blue tide occurs annually.5–7) Although large amounts of sand-capping materials are necessary for improvement of bottom sediments and backfilling of dredging sites, which are one of the causes of blue tide, use of industrial by-products as a substitute for natural sand and stone is demanded from the

* Corresponding author: E-mail: a-hayashi@hoshi.ac.jp
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viewpoint of protection of the natural environment. It has been reported that steelmaking slag, which is one candidate material, is more effective than natural materials in suppressing sulfide generation. The authors previously confirmed the effectiveness of steelmaking slag in decreasing the concentration of solved sulfides in an experiment in which steelmaking slag was added to artificial seawater containing sulfides. Based on an analysis of the reaction product of steelmaking slag and sulfide ions, the possibility that the Fe content in steelmaking slag decreases sulfides was suggested. Peaks consistent with sulfate ions (SO$_4^{2–}$) and simple sulfur were confirmed in the results of an X-ray absorption fine structure (XAFS) analysis of the formed product (suspended matter captured on filter paper). However, in those experiments, it was not possible to verify whether the peaks corresponding to those substances originated from sulfate ions (SO$_4^{2–}$) in the seawater and sulfur and sulfates in the steelmaking slag, or from the added sulfides. As a result, it was not possible to clarify the mechanism of suppression of dissolved sulfides in seawater by steelmaking slag.

Therefore, in the present paper, first, the reaction product of steelmaking slag and sulfide ions in artificial seawater was clarified. Following this, the elementary reaction of Fe contained in steelmaking slag and sulfide ions was considered under a condition which was not influenced by sulfate ions (SO$_4^{2–}$) by using an NaCl solution in place of seawater, and the mechanism responsible for suppression of dissolved sulfides by steelmaking slag was elucidated.

## 2. Experimental Method

### 2.1. XAFS and SEM-EDX Analysis of Reaction Product of Steelmaking Slag and Sulfide Ions in Artificial Seawater

310 ml of artificial seawater (Aquamarine; manufactured by Yashima Pure Chemicals Co., Ltd.), containing 2768 mg/L of sulfate, was aerated with nitrogen gas to a dissolved oxygen (DO) concentration of 2 mg/L or less, after which 30 mg-S/L of sodium sulfide·9 hydrate (Na$_2$S·9H$_2$O; manufactured by Kishida Chemical Co., Ltd., special grade) was dissolved in sodium chloride (NaCl) solution was added, and pH was adjusted to 8.2±0.1 using 1 mol/L of HCl. This artificial seawater was then poured gently into 250 ml polystyrene bottles until full. 0.08 mass% of steelmaking slag A, slag B (particle size ≤0.5 mm) shown in Table 1 or pure iron powder (particle size: 0.075–0.15 mm) was added, and the solution was stirred at 40 rpm with a rotary shaker at 20°C. The dissolved sulfide concentration was measured at specified points in time using a Kitagawa-type gas detection tube, and pH and oxidation-reduction potential (ORP) were measured after 22 hr. pH was measured by the platinum electrode method (Water Pollution Survey Guidelines 5.14) in accordance with JIS K0102 12.1, and the hydrogen electrode standard value was calculated using the single electrode potential of a reference electrode (Ag-AgCl/3.3 mol/L KCl). For comparison, an experiment was also performed without adding steelmaking slag or pure iron powder. Slag A is a steelmaking slag which was generated in the dephosphorization pretreatment process, and slag B is a steelmaking slag generated in the converter decarburization process.

Next, 1.0 mass% of steelmaking slag A, slag B (particle size ≤0.5 mm) shown in Table 1 or pure iron powder (particle size: 0.075–0.15 mm) was added to artificial seawater which had been adjusted and stirred in the same manner. After 24 hr X-ray absorption fine structure (XAFS) analysis (beamline BL-10 of the Ritsumeikan University Research Organization for Science and Engineering Synchrotron Radiation Center) of the K-edge of sulfur was performed for the suspended matter and slag recovered on the filter paper. For the XAFS analysis, the same conditions were applied as in Asaoka et al. In the experiment using slag A, elementary mapping and elementary analysis by scanning electron microscopy–energy dispersive X-ray spectrometry (SEM-EDX) were performed for the suspended matter.

### 2.2. XAFS Analysis of Reaction Product of Steelmaking Slag, Iron Oxide, Pure Iron Powder, and Sulfide Ions in Aqueous NaCl Solution

19.3 g of sodium chloride (manufactured by Kishida Chemical Co., Ltd., special grade) was dissolved in 310 ml of pure water, and the solution was aerated with nitrogen gas to a dissolved oxygen (DO) concentration of 2 mg/L or less. A 22.5 mg-S/L solution was then prepared by adding Na$_2$S·9H$_2$O, and pH was adjusted to 8.2±0.1 by dripping 1 mol/L of HCl into the prepared solution. 1.0 mass% of steelmaking slag A (particle size ≤0.5 mm), pure iron powder (particle size: 0.075–0.15 mm), or FeO powder (particle size ≤0.1 mm) shown in Table 1 was added to the NaCl solution, respectively, and the solution was stirred at 40 rpm with a rotary shaker at 20°C. After 24 hr, the suspended matter which had formed in the NaCl solution was filtered, and XAFS analysis of the K-edge of sulfur was performed for the suspended matter, slag, iron powder, and FeO powder recovered on the filter paper. The details of the XAFS analysis are as follows. Synchrotron radiation from bending magnets was diffracted with a Si (111) 2 crystal spectroscope, and XAFS measurement was performed with a specimen placed in an He-replaced specimen chamber. The specimen was fixed with two-sided tape to the center of a copper plate with a hollow (15 mm). The beam was irradiated on the...
specimen at an angle of 20°, and the fluorescence yield (FY) from the specimen before and after sulfide ion adsorption was measured using a silicon drift detector (SDD).\(^{10}\)

3. Results and Discussion

3.1 Reaction of Steelmaking Slag and Sulfide Ions in Artificial Seawater

0.08 mass% of steelmaking slag or iron powder was added to artificial seawater containing sulfide ions, and the change over time in the sulfide ions in the artificial seawater was obtained. The results are shown in Fig. 1. The sulfide concentration in the solution decreased to below the detection limit 3 hr after addition of steelmaking slag A and 22 hr after addition of steelmaking slag B or pure iron powder. On the other hand, in the blank test with no addition of any kind, the decrease in the concentration of sulfide ions in the solution was limited to 20 ppm after 24 hr, in spite of oxidation by residual dissolved oxygen/oxygen pickup during measurement and decrease due to adhesion on the container. Thus, the sulfide ion suppression effect of steelmaking slag and iron powder was confirmed from this figure. Table 2 shows pH and ORP after 22 hr. In comparison with the blank test, ORP increased with addition of the pure iron powder, steelmaking slag B, and steelmaking slag A, in that order.

It is considered that the reason why the decrease in sulfide ions by addition of steelmaking slag A was faster than that with steelmaking slag B, as shown in Table 1, was that the total iron content (T-Fe) and metallic iron content (M-Fe) of steelmaking slag A were both high in comparison with steelmaking slag B, being 51.7% and 37.1%, respectively, and thus this facilitated the reaction with sulfide ions. Furthermore, it is considered that compared with the pure iron powder, the more rapid decrease in the sulfide ion concentration with steelmaking slag A was attributed to the fact that the oxidation-reduction potential (ORP) of slag A in the solution was high in comparison with the pure iron powder, as shown in Table 2, and thus high level of ORP accelerated the oxidation of dissolved sulfide. It is known that in marine sediments rapid reaction may occur between Fe-oxides as well as Mn-oxides and dissolved sulfide.\(^{11,12}\) Therefore, Fe oxides and Mn oxides in slag A was also considered to accelerate the oxidation of dissolved sulfide.

Figure 2 shows an optical microscope photograph of the suspended fine particles recovered on the filter paper in the experiment using steelmaking slag A. The results of elementary mapping of these suspended fine particles by SEM-EDX are shown in Fig. 3. While the distributions of Fe and S show good agreement in this figure, virtually no agreement can be seen between the distribution of Ca and the distributions of Fe and S. The results of elementary analysis of the suspended fine particles are shown in Fig. 4. Peaks of S and Fe can be confirmed. This is the same result as that obtained by electron probe microanalyser (EPMA) elementary mapping of the cross section of slag particles after reaction, which was presented in a previous report.\(^9\)

Figure 5 shows the results of XAFS analysis of the K-edge of sulfur in the suspended substance on the filter paper. From this figure, the existence of peaks near those of FeS, FeS\(_2\), and simple sulfur, and a peak coinciding with sulfate were confirmed from the suspended fine particles obtained in the experiment using steelmaking slag A; a peak near the peak of sulfate was confirmed from the suspended fine particles in the case of steelmaking slag B; and a peak coinciding with FeS and a peak near that of sulfate were confirmed from the suspended fine particles in the case of the pure iron powder.

Figure 6 shows the XAFS analysis results of the K-edge of sulfur for the steelmaking slag and pure iron particle surface after reaction. Peaks coinciding with peaks of FeS and sulfate were confirmed on the surface of steelmaking slag A, and a peak consistent with sulfate was confirmed on steelmaking slag B. On the other hand, peaks corresponding to FeS, FeS\(_2\), simple S, and sulfate could not be detected on the particle surface of the pure iron after reaction.

The results of the XAFS analysis of the K-edge of sulfur for the suspended fine particles and particle surfaces after reaction are summarized in Table 3. In this table, the open
circle (○) mark indicates agreement with the peak, and the triangle (△) mark indicates that a near-peak was confirmed. Because steelmaking slag A has a high content of total iron and also has a high content of metallic iron, it is considered that sulfide ions change to the forms of FeS, FeS$_2$, simple S, and sulfate, and as a result, peaks coinciding with or near those peaks were observed in the suspended fine particles after reaction. In the case of steelmaking slag B, based on the low metallic iron content and high oxidation-reduction potential of the solution, it is thought that the larger part of the sulfide ions changed to the form of sulfate, and therefore a near-peak of sulfate was observed in the suspended fine particles after reaction. Peaks coinciding with sulfate were observed from the particle surfaces after reaction with both steelmaking slag A and B, but it was not possible to decide whether these were sulfate in the slag, dissolved sulfate of artificial seawater, or sulfate resulting from sulfite oxidation. With the pure iron powder, it is considered that eluted Fe ions and sulfide ions reacted to form FeS, and a peak coinciding with this peak was observed in the suspended

Fig. 3. SEM image and EPMA elemental maps of the suspended fine particles in the sulfide solved artificial seawater added with slag-A (S, Ca, Fe).

Fig. 4. SEM image and XRF signals obtained by EDX of the suspended fine particles in the sulfide solved artificial seawater added with slag-A.

Fig. 5. K-edge XAFS of the suspended fine particles in the sulfide solved artificial seawater added with slag-A, slag-B and iron powder respectively.
fine particles after reaction. The fact that no peak of sulfate was observed from the particle surface of the pure iron powder after reaction is attributed to the strong reducing power of the surface of the pure iron powder.

Based on these results, the decrease in sulfate concentration with steelmaking slag A is attributed to a process in which the metallic iron and iron oxides in the slag reacted with sulfide ions to form FeS and FeS₂, and due to the accompanying increase in ORP, sulfide ions were oxidized to sulfate ions. On the other hand, with steelmaking slag B, the fact that ORP was increased by oxides in the slag, and as a result, sulfide ions were oxidized to sulfate ions, is considered to be the main factor in the decrease in sulfate concentration.

3.2. Reaction Products of Steelmaking Slag, Iron Oxide, Pure Iron Powder, and Sulfide Ions in NaCl Solution

Sulfate was confirmed as a reaction product, however, it is also considered possible that this compound originates from sulfate ions in seawater and/or sulfur and sulfate in steelmaking slag. To eliminate sulfate ions in seawater, reaction experiments using a NaCl solution were carried out and the reaction product was identified.

The results of XAFS analysis of the $K$-edge of sulfur for the suspended fine particles (reaction product) on the filter paper are shown in Fig. 7. Peaks consistent with FeS₂ and simple S and a peak near that of sulfate can be confirmed from the reaction product of steelmaking slag A; peaks near those of FeS₂ and simple S and a peak consistent with sulfate can be confirmed from the reaction product of FeO; and peaks near those of FeS₂, simple S, and sulfate can be confirmed from the reaction product of pure iron powder.

**Figure 8** shows the results of XAFS analysis of the $K$-edge of sulfur for the surfaces of steelmaking slag A, FeO, and pure iron powder after reaction. In the particles of steelmaking slag A after reaction, peaks near those of FeS₂ and simple S and a peak near that of sulfate can be confirmed. With the pure iron powder, a peak near that of FeS was observed.

In the results of addition of FeO to a solution prepared by
adding sulfide to an aqueous solution of NaCl which did not contain sulfate, peaks near those of FeS$_2$ and simple S and a peak consistent with sulfate were observed from the suspended fine particles, whereas, in the results of addition of pure iron powder, peaks near those of FeS$_2$, simple S, and sulfate were obtained from the suspended fine particles. From these results, the decrease in sulfide in the solution is considered to be due to a change to multiple forms, namely, FeS$_2$, simple S, and sulfate ions. Accordingly, part of the sulfate observed from the suspended fine particles which formed as a result of addition of slag containing metallic iron and iron oxide is considered to have been formed by oxidation of hydrogen sulfide in the solution.

The results of XAFS analysis of the K-edge of sulfur for the suspended fine particles and particle surfaces after reaction are shown in Table 3. Because slag A has a high content of FeO, similar peaks were observed with the suspended fine particles and particle surfaces after the reactions involving slag A and FeO, respectively. Moreover, since slag A has a high content of metallic iron, the peaks after reaction with slag A are also similar to those observed from the suspended fine particles after reaction with pure iron powder. However, it is thought that peaks of FeS$_2$, simple S, and sulfate were not observed on the surface of the pure iron powder due to the strong reducing power of the powder surface.

### 3.3. Oxidation-Reduction Potential-pH Diagram for Artificial Seawater Containing Sulfide Ions

The reaction products were clarified for the cases where steelmaking slag, pure iron powder, and FeO were reacted with seawater and an NaCl solution containing solved NaS. However, in order to clarify the mechanism responsible for the formation of these reaction products, it is necessary to know the state of existence of each element in those solutions. In the present research, this was studied using the oxidation-reduction potential-pH diagram (Eh-pH diagram).

The Eh-pH diagram for sulfur in artificial seawater containing 20 ppm of sulfide ions is shown in Fig. 9. Figures 10 and 11 show the Eh-pH diagrams for S and Fe, respectively, in artificial seawater containing 5 ppb of Fe and 20 ppm of sulfide ions. These Eh-pH diagrams were prepared using a thermodynamic equilibrium calculation program (The Geochemist’s Workbench Essentials 8.0, HULINKS).

In these calculations, the pressure and temperature were 1 013 hPa and 25°C, respectively, and the ionic strength of the main ions in the seawater were assumed to be Na: 0.286, Mg: 0.0129, Ca: 0.0021, and Cl: 0.362, referring to the activity coefficients reported by Leyendekkers. Based on the sulfide concentration of interstitial water in the bottom sediments at Hiroshima Bay (0.01–47 ppm), 20 ppm was used as the concentration of sulfide ions, assuming an actual sea area with a high sulfide concentration, and 0.00069 was used as the ionic strength of S. The concentration of Fe was calculated at 5 ppb, assuming a high dissolved Fe concentration, referring to the concentration of dissolved Fe in summertime of water overlying the bottom sediments in Kawasaki Bay (measured at 2 locations, 7 ppb and 15 ppb, respectively) and the concentration of dissolved Fe in Seto Inland Sea (0.3–6.2 ppb).

From Fig. 9 under a reducing atmosphere with a low ORP in a condition in which Fe does not exist, it is considered that the sulfides in the solution in the form of HS$^-$ at the pH (8.2) of ordinary seawater exist, and under an oxidizing atmosphere with a high ORP, the sulfides exist in the form of sulfate ions. On the other hand, from Fig. 10, in a state in which Fe exists, it is considered that sulfide forms troilite (FeS) and pyrite (FeS$_2$) under a reducing atmosphere with a low ORP, whereas, under an oxidizing atmosphere with a
high ORP, the sulfides exist in the form of sulfate ions. Where Fe is concerned, from Fig. 11, under a reducing atmosphere where sulfide exists in the form of HS\(^-\), it is thought that sulfide forms pyrite (FeS\(_2\)) and under an oxidizing atmosphere where sulfides exist in the form of sulfate ions, Fe exists in the form of hematite and Fe ions.

### 3.4. Mechanism of Sulfide Ion Suppression in Seawater by Steelmaking Slag

From the results of these experiments and the Eh-pH diagrams, in the low DO concentration region, it is considered that the Fe contents eluted from steelmaking slag, pure iron powder, and FeO react with dissolved sulfide ions in accordance with the reactions in Eqs. (1), (2), and (3)\(^{16,17}\) and form insoluble substances such as troilite (FeS), pyrite (FeS\(_2\)), etc.

\[
\text{HS}^- + \text{Fe}^{2+} \rightarrow \text{FeS} + \text{H}^- \quad (1)
\]

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

\[
\text{FeS} + \text{S}^0 \rightarrow \text{FeS}_2 \quad (3)
\]

Asaoka et al. reported\(^{10}\) that the possibility of sulfide oxidation by Fe in granulated coal ash and the formation of pyrite as a mechanism of sulfide ion suppression by granulated coal ash, and the present research results are in agreement with this. In the high DO concentration region, it is considered that sulfate ions (SO\(_4^{2-}\)) are formed by the reaction in Eq. (4)\(^{18}\).

\[
\text{HS}^- + 2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+ \quad (4)
\]

Mixed experiments using dissolved sulfide in artificial seawater and an NaCl solution, and steelmaking slag, FeO, and iron powder were performed with solutions in which oxygen was deaerated with nitrogen. However, it is considered possible that FeSO\(_4\) was formed by the reaction in Eq. (5)\(^{19}\) as a result of contact of those specimens with the air in the process of performing the XAFS analysis.

\[
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \quad (5)
\]

In this research, (1) the existence of FeS and FeS\(_2\) was confirmed by XRF and XAFS in laboratory experiments using deaerated solutions, and (2) from the Eh-pH diagram in Fig. 11, in a condition in which Fe exists, sulfur exists in an equilibrium state in the forms of troilite (FeS) and pyrite (FeS\(_2\)) under a reducing atmosphere with a low oxygen-reduction potential (ORP). Based on these two facts, it is considered that HS\(^-\) and H\(_2\)S react with Fe to form FeS and FeS\(_2\) under anoxic or extremely low DO concentration conditions. Furthermore, from the experimental result that FeS\(_2\) formed when FeO was added to the NaCl solution containing sulfide, it is considered that iron oxide reacts with HS\(^-\) to form FeS\(_2\) under a condition where the oxygen concentration is extremely low. On the other hand, if oxygen is supplied from the atmosphere or from oxides, it is thought that sulfide is oxidized to sulfate ions, and FeS and FeS\(_2\) are oxidized to iron oxide and sulfate.

Based on the results of the study presented above, the following two mechanisms of suppression of sulfide generation by steelmaking slag are conceivable. The first is a mechanism in which sulfide generation is suppressed by formation of FeS and FeS\(_2\) by reaction of the metallic iron and iron oxide contained in the slag with sulfide ions. The second is a mechanism in which the high level of ORP caused by steelmaking slag promotes the oxidation of sulfide and suppressed the generation of sulfate as shown in Table 2 and Fig. 1. The second mechanism is consistent with the results of a demonstration experiment at the Keihin Canal, Port of Kawasaki, in which the ORP of the bottom sediments where steelmaking slag was laid was greatly improved in comparison with that of the natural seabed.\(^{30}\) It is also in agreement with the result that ORP is increased and sulfide ions in artificial seawater are oxidized when steelmaking slag is added under a condition in which the solution was deaerated with nitrogen, and the solution was also kept in a sealed condition as shown in Table 2 and Fig. 7.

According to a study carried out by Kanaya and Kikuchi at a brackish lagoon (Gamo Lagoon, Sendai, Japan) and a river-affected lagoon (Idoura Lagoon, Sendai Bay, Japan), in summer, generation of sulfides was observed in the surface layer of the bottom sediments at Gamo Lagoon, where the average of total Fe concentration in the sediments is 466 \(\mu\text{molg}^{-1}\text{drywt}\) (2.6 mass%), but through the year, generation of sulfides was not observed at Idoura Lagoon, where the average concentration of total Fe in the bottom sediments is 690 \(\mu\text{molg}^{-1}\text{drywt}\) (3.85 mass%).\(^{20}\) According to a study by Canfield, in summer, generation of sulfides was observed in the surface layer of the bottom sediments in the sea near Long Island Sound, USA, where the average of total Fe concentration in the sediments was 2.22–3.25 mass%, but through the year, generation of sulfides was not observed in the Mississippi Delta region of the Gulf of Mexico, where the average concentration of total Fe in the bottom sediments was 3.91–4.44 mass%\(^{11}\).

From these studies, it is known that Fe in sediments can reduce sulfides in pore water and in sediments. And it implies that generation of sulfides in sediments would be reduced if Fe ions can be supplied by laying steelmaking slag, which usually has an iron content close to 20%, in bottom sediments.

According to a study carried out by T. F. Rozan et al. at Rehoboth Bay Delaware (U.S.A.), in August, FeS in the sediment was more than 80 \(\mu\text{molg}^{-1}\text{drywt}\) and the concentration of Fe (III) oxides was less than 30 \(\mu\text{molg}^{-1}\text{drywt}\). In April, FeS in the sediment was less than 40 \(\mu\text{molg}^{-1}\text{drywt}\) and Fe (III) oxides were more than 120.\(^{21}\)

It is considered that under the oxygen-deficient condition in summertime, H\(_2\)S and HS\(^-\) combine with metallic iron and iron oxides to form FeS and FeS\(_2\), thereby suppressing generation of sulfides, and in wintertime, when the dissolved oxygen concentration in seawater increases, FeS and FeS\(_2\) are oxidized to form iron oxides and sulfate ions. Therefore, it is expected that generation of H\(_2\)S in bottom sediments can be suppressed throughout the year by repetition of this cycling process. This estimate is in agreement with the results of measurements in various parts of the world showing that the sulfide concentration of bottom sediments is low in marshes with high concentrations of Fe,\(^{11,12,20-23}\) and the results of research on the circulation of iron, manganese, sulfur, and phosphorus in coastal shallows.\(^{12,23}\)
Based on the above, it is considered that H$_2$S generation can be suppressed and blue tide can be prevented throughout the year by laying steelmaking slag in oxygen-deficient bottom seawater and the bottom sediments of inner bays and former dredging sites, where the content of organic matter is high and H$_2$S is easily generated in summertime. Field experiments, in which steelmaking slag is laid in actual seawaters where hydrogen sulfide generation causes problems, and investigation of the effects of laying the steelmaking slag are topics for a future study.

4. Conclusion

Suppression of sulfide ions in solutions by addition of steelmaking slag, FeO, and metallic iron was investigated with a solution in which sulfides were added to artificial seawater containing sulfate and a solution in which sulfides were added to an aqueous solution of NaCl that did not contain sulfate. As a result, the following points were clarified.

(1) When FeO was added to the solution in which sulfides were added to an aqueous solution of NaCl that did not contain sulfate, sulfide ions were oxidized and formed sulfate ions.

(2) When steelmaking slag was added to artificial seawater containing sulfides, 1) Fe contained in the steelmaking slag reacted with sulfide ions to form sulfides of iron, and 2) a shift to an oxidizing atmosphere was promoted, and as a result, sulfide ions were oxidized to form sulfate ions.

(3) Based on the above results, 1) Fe contained in steelmaking slag and sulfide ions react to form sulfides of iron, and 2) the shift to an oxidizing atmosphere is promoted and sulfide ions are oxidized to sulfate ions. It is considered that addition of steelmaking slag suppresses sulfide ions in artificial seawater by these two mechanisms.

(4) These results suggested the possibility that generation of hydrogen sulfide can be suppressed by laying steelmaking slag in bottom sediments.

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