Short communication

Removal of hydrogen sulfide with steelmaking slag by concurrent reactions of sulfide mineralization and oxidation

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ABSTRACT

This study experimentally revealed the entire mechanisms of mineralization and oxidation of H_2S by steelmaking slag. After adding steelmaking slag to an artificially prepared H_2S solution, white precipitates were generated, and were identified as elemental sulfur by X-ray absorption fine structure spectra. Sulfate ion was also detected in the solution, but in small amounts. In addition, FeS was identified on the surface of the steelmaking slag. An increase in the oxidation–reduction potential implies the oxidation of H_2S by the steelmaking slag, resulting in the formation of oxidized sulfur compounds. We confirmed that steelmaking slag can effectively remove H_2S through oxidation as well as through its mineralization to FeS and that these processes are promoted by both Fe and Mn originating from the slag.

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1. Introduction

The formation of hypoxic water in the bottom layer of enclosed water bodies has been observed worldwide (Gianni et al., 2011; Wu et al., 2013). In addition to the consumption of dissolved oxygen (DO) due to the decomposition of organic matter, hypoxia of the bottom water can occur due to the consumption of DO by reductants such as hydrogen sulfide (H_2S; Endo and Shigematsu, 2010), which is generated by sulfate-reducing bacteria under hypoxic conditions (Ito, 1996). Because of the acute toxicity of H_2S, the survival rate of benthic organisms is decreased (Marumo and Yokota, 2012). Thus, the generation of H_2S should be suppressed in order to improve the quality of the benthic layer of enclosed water bodies.

Steelmaking slag is produced when steel is manufactured from pig iron. It is commonly utilized as a raw material in the form of coarse aggregates for concrete and roadbed construction. Recent studies have shown some of the advantages of steel slag, such as the

removal of phosphorus (Li et al., 2013) and wastewater treatment (Wang et al., 2010).

The present study evaluates the effect of steelmaking slag on improving the sediment quality by reducing H_2S, which binds to iron, forming FeS and FeS_2 (Hayashi et al., 2012a,b). Furthermore, H_2S forms not only FeS but also sulfur ($S^{(0)}$), MnS, and sulfate (SO_4^{2-}) when reacting with steelmaking slag (Kim et al., 2012). The objective of the present study is to understand the primary processes and mechanisms involved in H_2S removal, which may be mineralization and oxidation, using steelmaking slag.

2. Materials and methods

2.1. Steelmaking slag

The steelmaking slag had a diameter of 0.85–2.0 mm and was provided by JFE Steel Corporation, Ltd. (Tokyo, Japan). It was mainly composed of SiO_2, CaO, T-Fe, MnO, and Al_2O_3 (Table 1). The mineral forms were identified as FeO, $CaO-SiO_2-Al_2O_3$. Glass was not identified because the slag was not quenched.

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Table 1
Chemical composition of the steelmaking slag used in the present study.

Substance	Average ± SD (%)	Substance	Average ± SD (%)
SiO_2	32.0 ± 1.4	MgO	4.33 ± 0.8
CaO	31.5 ± 0.4	P_2O_5	3.42 ± 0.1
T-Fe	15.6 ± 1.2	TiO_2	1.16 ± 0.0
MnO	6.35 ± 0.6	S	0.12 ± 0.0
Al_2O_3	4.88 ± 0.6	Na_2O	0.73 ± 0.1

2.2. H_2S removal experiments

Experiments were carried out for 1 week using 150 mL glass vials containing 100 mL H_2S solutions with concentrations of 0, 25, 50, 75, 100, and 150 mg S/L in order to observe the differences in the reactions with steelmaking slag at different H_2S concentrations. The test period (1 week) was selected based on the decreasing trend observed in the preliminary experiments (data not shown). The H_2S solution was prepared as follows: 1 M analytical grade, autoclaved Tris–HCl buffer (Wako Pure Chemical Industries, Osaka, Japan) was added to Milli-Q water that had been deaerated with N_2 gas to reach a final concentration of 30 mmol/L to maintain a stable pH in the solution. One aliquot of analytical grade $Na_2S·9H_2O$ (Nacalai Tesque, Kyoto, Japan) was then dissolved in the deaerated water. The H_2S solution was slowly dispensed into the vials and 0.2 g steelmaking slag was added gently. Each vial was plugged with a rubber cork and sealed with an aluminum cap after displacing the air in the head space with N_2 gas. The vials were then agitated at 40 rpm at 25 °C in a water bath for 1 week, and the concentrations of H_2S in the solution were determined with a detection tube (200SA or 200SB; Komyo Rikagaku Kogyo, Kanagawa, Japan). The pH and oxidation reduction potential (ORP) were measured with a pH electrode (F-22; Horiba, Ltd., Kyoto, Japan) and an ORP electrode (RM-20P; DKK-TOA Corporation, Tokyo, Japan), respectively. The ORP value was converted to the Eh value [Eh = ORP + 206 − 0.7(t − 25); t: water temperature (°C)]. Control experiments were also carried out without using the steelmaking slag. All experiments were performed in triplicate.

The remaining H_2S was scavenged by adding zinc acetate to form ZnS, as described by Ito (1996), to determine the sulfate (SO_4^{2-}) concentrations. After the precipitates settled, the supernatant solution was filtered through a hydrophilic polyvinylidene difluoride filter with a pore size of 0.45 μm (Millex; EMD Millipore Corporation, Billerica, Massachusetts, USA). The pH was then adjusted to neutral, and the SO_4^{2-} concentrations were determined using an ion chromatograph (ICS-200; Dionex, Sunnyvale, CA, USA).

The total dissolved Fe and Mn concentrations were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Optima 7300DV; PerkinElmer, Waltham, MA, USA) for the filtered samples, to which HNO_3 was added to obtain a final concentration of 3%.

Because two types of precipitates (white and black) were formed in the solution, and color changes in the slag surface were also observed, and additional experiments and analyses were conducted as described below.

2.3. X-ray absorption fine structure analyses and data processing

In order to analyze the precipitates and substances formed on the slag surface, which become black, additional experiments were carried out under the same conditions (1 week in a 50 mg S/L solution). The white precipitates formed in the solution were collected through a glass fiber filter (Whatman GF/F; Whatman Plc,

Maidstone, Kent, UK). The samples for the X-ray absorption fine structure (XAFS) analyses were prepared by drying the samples in a nitrogen atmosphere. Iron, manganese, and sulfur K-edge XAFS spectra measurements and their data processing were conducted according to a previous report (Asaoka et al., 2012) using BL3 at the Ritsumeikan SR Center, Japan, and BL11 at the Hiroshima Synchrotron Research Center (HiSOR), respectively.

3. Results

3.1. Results of H_2S removal experiments

The concentration of H_2S decreased under all the experimental conditions compared to control (Fig. 1a). Sulfate was detected in small amounts after the experiment (ca. 1/20 of the H_2S concentration), and initial H_2S concentrations of 0, 100, and 150 mg S/L in the solutions, SO_4^{2-} concentrations were higher compared to control (Fig. 1d).

During the experiment, the pH values increased by 0.2–0.5 compared to control (Fig. 1b). The Eh values of the slags increased up to +148 mV from −109 mV and +238 mV from −126 mV at initial concentrations of 25 and 50 mg S/L, respectively, while the Eh increase in the control was not statistically significant (Fig. 1c).

The Fe and Mn concentrations in the solution determined by ICP-AES were 0.03–0.60 mg/L and 0.25–0.65 mg/L, respectively (Fig. 2). Both the elements behaved similarly, showing high concentrations under low (<50 mg S/L) H_2S concentrations and low concentrations under high (>75 mg S/L) H_2S concentrations.

White precipitates were generated in the 25 and 50 mg S/L solutions. In these solutions, no H_2S was detected in either the gas or liquid phases. White precipitates were not observed in the control. Furthermore, a yellowish color was observed in all the experimental solutions, but this color disappeared upon the formation of white precipitates under the conditions with initial H_2S concentrations of 25 and 50 mg S/L. The yellowish color did not disappear under higher (>75 mg S/L) H_2S concentrations.

Black substances were also observed on the surfaces of several slag particles. They were easily removed from the slag surface by shaking.

3.2. Results of X-ray absorption fine structure analyses

The sulfur K-edge XAFS spectra of the standard substances and samples are shown in Fig. 3a the slag after the experiment showed a peak at 2470 eV, which is identified as that of FeS from the spectra of the standards (Fig. 3a). On the other hand, a peak at 2472 eV was detected for the precipitates, which was identified as $S^{(0)}$. Furthermore, $S^{(0)}$ and FeS were not observed on the surface of the initial steelmaking slag (Fig. 3a).

The iron K-edge XAFS spectra of the standard substances and samples are shown in Fig. 3b. The iron K-edge spectra of the initial slag can be successfully fitted by a combination of FeO 48%, iron (III) hydroxide 18%, and iron (II) hydroxide 34%. On the other hand, the iron K-edge spectra of the slag after the experiment can be successfully fitted by a combination of FeO 74% and iron (III) hydroxide 26%.

The manganese K-edge XAFS spectra of the standard substances and samples are shown in Fig. 3c. The manganese K-edge spectra of the initial slag can be successfully fitted by a combination of $MnSO_4$ 58%, MnO 24%, and MnO_2 18%. On the other hand, the manganese K-edge spectra of the slag after the experiment can successfully be fitted by a combination of initial slag 32%, $MnSO_4$ 48%, and MnO 20% with no MnO_2 that was observed on the initial slag.