Technical Report

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Study on Environmental Impact Evaluation of Steelmaking Slag Using in Coastal Sea Area

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Abstract

Steelmaking slag came to be used in a marine environment and safety issue of slag is a matter of concern. We are trying to provide the safety information of the slag material. Experimental facility with mesocosm aquariums was constructed in RE center in order to clarify the mechanisms for efficacy and to evaluation of the safety for environmental organisms.

1. Introduction

Nippon Steel & Sumitomo Metal Corporation has been developing a new technology that aims to use the advantageous characteristics of steelmaking slag to improve the environment of sea areas. Because of its unique physical properties, steelmaking slag has attracted growing attention as a material for civil works. Steelmaking slag also has come to be used as a material for restoring seaweed grounds damaged or lost due to sea desertification, as the iron contained in the slag serves as fertilizer for the seaweeds. In addition, steelmaking slag is being put into practical use as a material that helps improve the environment of sea areas. For example, when soft seabed sediments are mixed with steelmaking slag, they increase in strength as a result of hydration. As another example, steelmaking slag is expected to restrain the elution or formation of environmental pollutants such as phosphorus and sulfides.

In applying steelmaking slag in an actual sea area, however, we consider it important to discuss the scope of the favorable effect it exerts and collect as much data as possible about the safety of steelmaking slag, that is, the influence of the slag on the ecosystem of the sea area. Nevertheless, since the weather and climatic conditions of sea areas are subject to wide fluctuations, it is not always easy to determine the effect of steelmaking slag accurately. Therefore, the company has verified it using large water tanks installed in its experimental facility. With respect to the safety of steelmaking slag, too, it has been studied from the biological and ecological standpoints. In this report, we shall describe the company's activity to evaluate the usefulness and safety of steelmaking slag applied in actual sea areas.

2. Discussion on the Effect of Steelmaking Slag Used in an Actual Sea Area and the Extent Thereof

Concerning the restoration of seaweed grounds using a slag-based material to supply the needed iron and the improvement of the environment of sea areas using CaO-improved dredged soil, the effect of steelmaking slag and their working have been verified by various indoor experiments. On the other hand, attempts have been made to evaluate the effects of restoration/improvement works performed in sea areas on a small scale or on full scale by field investigations on a continual basis. However, several of those attempts failed because of wide fluctuations of the weather and climatic conditions of the sea areas.

Therefore, employing the set of experimental water tanks that permits the simulation of the actual sea environment with minimum fluctuations of natural conditions, we attempted to verify the usefulness and effect of applying a slag-based materiel in a sea area and to interpret the material dynamics in sea areas on the basis of quantitative data obtained by simulations.

2.1 Study of usefulness under simulated sea environment

The experimental water tank facility for simulating the environment of sea areas, installed in 2009 in the RE Center in Futtsu City, Chiba Prefecture, is housed in a glass structure to admit ample sunlight (**Photo 1**). It accommodates two FRP water tanks—a tank used to study the restoration of seaweed grounds by the supply of iron (hereinafter the seaweed ground water tank; **Photo 2** (a)) and a tank used to study the improvement of the environment by the use of CaO-improved soil (hereinafter the shoal water tank; Photo 2 (b)).

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Photo 1 Photograph of apparatus of the mesocosm facility

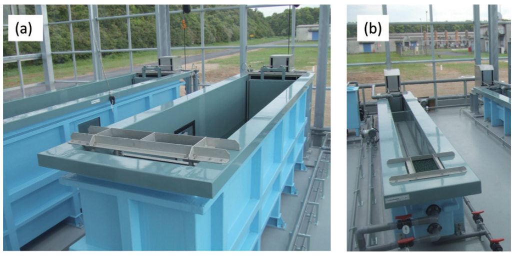

Photo 2 Mesocosm facility
(a) Seaweed grown tank, (b) Shallow seabed tank

2.1.1 Verifying the effect of steelmaking slag on the growth of seaweeds and the safety of steelmaking slag using the seaweed ground water tank

The seaweed ground water tank consists of the main tank (inside dimensions: 1 m (W) × 5 m (L) × 1.6 m (D)) equipped with a wave-making device and the reservoir (capacity: about 8 m^3) connected to the main tank. By letting seawater flow between the reservoir and the main tank, it is possible to reproduce the tidal movement in the water tank system. The system can be operated with seawater not circulated, that is, by discharging the seawater from the tank (about 10 m^3 during experiment) at low tide and by supplying fresh seawater to the tank at high tide. In the experiment by which to verify the effect of slag-based fertilizer, however, the system was operated with the seawater fully circulated in order to grasp the material balance.

First, a slag-based fertilizer (Vivary™ Unit) was put into one of the two seaweed ground water tanks into which surface seawater of Tokyo Bay was led. Then, both tanks were operated with the seawater circulating while they were subjected to artificial waves and tidal movement (12-h cycle), and the difference between them was observed. The quality of water in each tank was measured on a continual basis, and the supply of nutrients from the fertilizer and the uptake of those nutrients by seaweeds were studied. Laver nets onto which conchospores of red algae (*Pyropia yezoensis*) had been settled were installed in the two tanks and the condition of growth of the laver in the tanks was observed. On the 16th day from input of the fertilizer, leaf bodies with leaf lengths less than 100 μm were observed in both tanks, though the color of leaf bodies in the experimental tank was somewhat thicker than in the control tank. The condition of laver growth on the 48th day from input of the fertilizer is shown in **Fig. 1**. Although a favorable growth of the laver in the experimental tank could be seen with an unaided eye, the growth of laver could not be observed at all in the control tank.[1)] A similar experiment was performed on green algae (*Monostroma nitidum*). The condition of growth about four months after start of the experiment is shown in Fig. 1. It could be confirmed that the growth of *Monostroma nitidum* was promoted by input of the slag fertilizer.

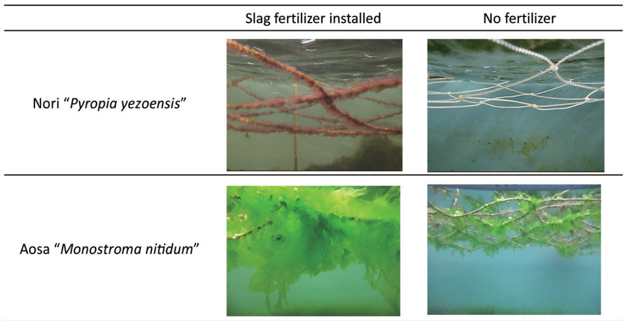

Fig. 1 Seaweeds grown in the experimental seawater tanks with or without slag fertilizer

The slag fertilizer used in the above experiments is a mixture of carbonated steelmaking slag and humus. It has been confirmed that the fertilizer elutes not only iron but also nitrogen, phosphorus, silicon, and other nutrients. Therefore, it cannot be concluded that the promoted growth of laver mentioned above is attributable only to iron. Although the effect of each individual nutrient will have to be studied, we could confirm that slag fertilizer promotes the growth of seaweeds. In addition, we recovered grown seaweeds and measured the contents of heavy metals in them. The measured heavy metal contents were compared with analytical values obtained in the past for *Pyropia yezoensis* and with those of the seaweeds in the control water tank for *Monostroma nitidum*. As the measured heavy metal contents of the experimental tank into which the slag fertilizer had been input were almost the same as the analyzed values, it was considered that there was not much possibility of the elution of heavy metals from the slag and the resulting biology concentration.

2.1.2 Verifying the effect of steelmaking slag to improve the sea environment using the shoal water tank

The shoal water tank consists of the main water tank (inside dimensions: 0.3 m (W) × 5 m (L) × 0.5 m (D)) equipped with a wave-making device and the reservoir tank (capacity: about 90 L) connected to the main tank. It allows for experimentation in a closed system with the seawater circulated between the main water tank and reservoir tank.

First, at the bottom of the shoal water tank, sediment collected from Tokyo Bay was laid out in the control section and sediment mixed with slag (CaO-improved soil) was laid out in the experimental section. Then, 600 L of artificial seawater was put into the tank. In the control section, the concentration of phosphorus in the form of phosphoric acid in the seawater significantly increased in the early stage of the experiment, and then, decreased with the multiplication of phytoplankton. The concentration of phytoplankton in the control section cyclically increased and decreased, whereas it remained low in the experimental section. With respect to the concentration of inorganic nitrogen, it increased in both sections in the early stage of the experiment. With the multiplication of phytoplankton, however, the concentration of inorganic nitrogen in the control section decreased, while it remained nearly the same in the experimental section. Presumably, the reason is that the multiplication of phytoplankton was restrained more effectively in the experimental section than that in the control section.

Thus, it was confirmed that when seabed sediment was improved by adding slag thereto, the elution of phosphorus from the sediment

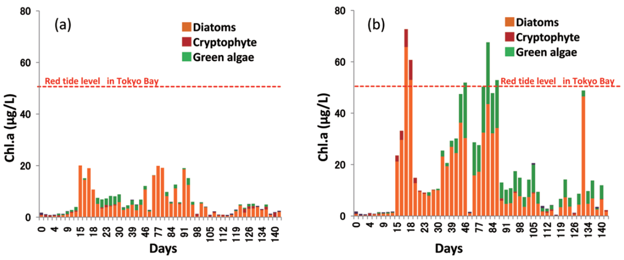

Fig. 2 Time-course changes of chlorophyll a in experimental tanks (a) CaO-improved soil, (b) Raw soil

decreased, and consequently, the multiplication of phytoplankton was restrained.[2] By the way, the fact that the addition of slag to seabed sediment helps restrain the elution of phosphorus from the sediment has also been verified by another experiment.[3]

Using seabed sediments collected from Osaka Bay, a similar experiment was performed to confirm the reproducibility of the above experimental results. As shown in **Fig. 2**, it was confirmed that while in the control section the multiplication of phytoplankton had increased to a red tide level, it had remained at low levels in the experimental section. Thus, using the shoal water tanks of SeaLabo I, we could confirm with high reproducibility the effect of slag fertilizer to help improve the environment of sea areas, i.e., restrain the occurrence of a red tide, though under extreme environmental conditions in a closed seawater-recycling system.

2.2 Developing seaweed grounds by supplying iron

The rate of iron elution from Vivary™ Unit has been experimentally obtained in the above experiment using the water tanks of SeaLabo I and other indoor experiments.[4] With respect to the elution of iron from a box filled with the slag fertilizer, too, attempts have been made to calculate the diffusion flux of iron (i.e., the mass of iron elution per unit time) from the fertilizer box using a fluid analysis technique[5] and to estimate the condition of iron diffusion in the vicinity of the fertilizer box.[6] Conversely, it can easily be estimated that when Vivary™ Unit is installed in an actual sea area, the iron eluted from the Unit will speedily be diffused by the waves and tides. Therefore, we considered it possible to estimate the extent of the effect of iron supplied from Vivary™ Unit by solving the problem of advection diffusion taking into account the topography and tidal currents of the sea area under consideration. So far, the efforts in that direction have been made in Hokkaido (Muroran, Suttsu),[7] Hyogo (Hirohata),[8] Oita (Saeki),[4] etc. However, there are still a number of unknowns about the requirements of fertilization for seaweeds, such as the suitable concentration of iron and the optimum timing of iron supply. Validating the analysis results obtained thus far will call for a detailed study in the future.

2.3 Restoring the environment by improving seabed sediments

The improvement of seabed sediments using slag and the development of shoals using CaO-improved soil were confirmed to have been effective not only to restrain the elution of phosphorus and the resulting red tide mentioned earlier but also to help restrain the occurrence of sulfides that cause the blue tide.[9] Using an "ecosystem model coupling floating-benthic systems"[10] that takes into consideration the above facts, an attempt was made to estimate the effect of improvement of the sea environment when a dredged bottom in Mikawa Bay was filled with a mixture of steelmaking slag and dredged soil, etc. As a result, it was found that there was no significant difference in water quality improvement effect between the land-filling materials used. However, the results of calculations showed that when the CaO-improved soil was used, the concentrations of hydrogen sulfide and other reducing substances that are very toxic to living things were lower than those when the unimproved dredged soil was used.[2]

3. Evaluation of the Safety of Using Steelmaking Slag in Sea Areas

3.1 Safety evaluation and product certification

When steelmaking slag is used in a sea area, it is subject to quality control compatible with the so-called seabed sediment standards, which are criteria[11] based on the Law on the Prevention of Marine Pollution and Maritime Disaster ("Marine Pollution Prevention Law") enacted as the standard relating to harmful substances in seabed sediments, in order to ensure that the elution of any substances from the steelmaking slag poses no problem from the standpoint of environmental conservation. In addition, studies have been made on various biological tests (e.g., guidelines on toxicity test for marine life[12]) proposed to assure that steelmaking slag has no adverse effects on the living things in the sea area in which the slag is used. Through the establishment of a quality control system and the accumulation of environmental impact assessment data mentioned above, the steelmaking slag products have secured the safety certification under the product safety and certification system enacted by the Japan Fisheries Cooperatives. In the sections that follow, we shall describe the development of slag materials for construction of new seaweed grounds and restoration of lost fishing grounds with the focus on the biological safety of those material.

3.1.1 Vivary™ series[13, 14]

As the slag-based materials for development of seaweed grounds, there are the Vivary™ Unit that is a fertilizer to supply iron and the Vivary™ Rock and Vivary™ Block that are artificial stones used as the bases of alga or fish reefs.

For the Vivary™ Series, it has been confirmed that the concentrations of harmful substances in an eluate prepared in accordance with Notification No. 14 of the Environment Agency meet the standards for seabed sediments mentioned above. In addition, in order to closely examine the effects on the ecosystems of the Vivary™ Series used in sea areas, acute toxicity tests on the groups of living things shown in **Table 1** were performed under the guidance of the Japan Fisheries Science and Technology Association. As a result, it was confirmed that the Vivary™ Series had no toxicity to the living

Table 1 Outline of the biological testing of slag

Category	Organism type	Test organism in this article	Test method
Group 1	Fish	Red seabream [*Pagrus major*]	96h-acute toxicity (survival)
Group 2	Shellfish	Abalone [*Haliotis discus*]	96h-acute toxicity (survival)
Group 3	Crustacean	Prawn [*Marsupenaeus japonicus*]	96h-acute toxicity (survival)
Group 4	Macroalgae	Seaweed [*Pyropia yezoensis*]	96h-acute toxicity (growth inhibition)
Group 5	Microalgae	Marine diatom [*Skeletonema costatum*]	72h-acute toxicity (growth inhibition)
Group 6	Pest organism	Red tide phytoplankton [*Heterosigma akashiwo*]	120h-effect on growth (growth stimulation)

things tested. In the above toxicity tests, the eluate was prepared by the tank leaching method in accordance with JIS K 0058-1: 2005 “Methods of Testing Chemical Substances Contained in Slags—Part 1.” The subject living things were kept directly in the eluate or in an eluate diluted with filtered seawater. After the lapse of a prescribed time, the survival rate of each group of subjects was calculated to determine the toxicity.

In securing the 2010 certification, the company carried out an acute toxicity test on each of four groups 1–4 (red sea bream, abalone, prawn, and laver) shown in Table 1. By the time of renewal of the certification in 2013, the company performed two additional tests to examine whether the Vivary™ Series would impede the growth of useful phytoplankton and influence the growth of plankton causing a red tide.

The test results for groups 1–3 are shown in **Table 2**.[15] In the tests, not only the eluate prepared by the tank leaching method using filtered seawater as the solvent (100% concentration in the table) but also an eluate diluted to 25%–75% with filtered seawater and the filtered water itself (0% concentration in the table) as the reference were used. The number of subjects per test section was 10 for the red sea bream, 10 for the abalone, and 20 for the prawn. In the acute toxicity test on red sea breams with Vivary™ Unit, an accidental death of one individual from the damage caused by a fight between individuals was observed in the 50% concentration section. In the other test sections, unexpected deaths or abnormal behaviors were not observed at all. Based on the above test results, it was judged that the Vivary™ Series (Unit, Rock, and Block) had no safety problems against marine life. In the acute toxicity tests on groups 4–6 too, neither an impediment to the growth of laver[16] and phytoplankton nor a marked multiplication of red tide-causing plankton was observed.

As a result of all that has been described above, the Vivary™ Series was certified in 2010 as a technology useful for developing seaweed grounds.

3.1.2 Calcium oxide soil improving material[17]

The material made from steelmaking slag for restoring the environment of fishing grounds is called calcium oxide (CaO) soil improving material. When the material is mixed in seabed sediments that are detrimental to fisheries in the locality, it makes those sediments coagulate or solidify. The mixture of CaO and sediment (CaO-improved soil) is a land-filling material aimed to restore the functions of fishing grounds.

For the CaO soil improver, as in the case of the Vivary™ Series, it has been confirmed that the concentrations of harmful substances in its eluate prepared in accordance with Notification No. 14 of the Environment Agency meets the standards for seabed sediments mentioned earlier. In addition, in order to make a close examination of the effects on the ecosystems of the sea area in which the CaO soil improver is used, biological tests have been performed on for the groups of living things shown in Table 1 under the guidance of Japan Fisheries Science and Technology Association. So far, the tests on groups 1–4 have been completed, proving that the CaO soil improver has no toxicity to the living things tested. Moreover, in view of the possibility that CaO-improved soil will be spread over a wide area of seabed, not only the acute toxicity but also the long-term safety of the CaO material was confirmed by a 30-day breeding test. Specifically, red sea breams and abalones were bred in seawater that was passed through a water tank into which CaO soil improver or CaO-improved soil had been input, and the 30-day survival rate, the presence or absence of abnormal behavior, and the contents of heavy metals at the end of the test were compared with those of red sea breams and abalones that were bred in seawater free of slag material (control section). As a result, it was confirmed that there was no significant difference between them.

In addition, in a sea area in which CaO-improved soil had been applied, fishes and shellfishes were collected and the compositions of nutrients and the contents of heavy metals of them were measured. There was no significant difference between those fishes/shellfishes and their counterparts collected in the control section. Thus, it was confirmed that even those fishes and shellfishes that were living in a sea area where CaO-improved soil had been applied were completely safe to eat.

In view of all the test results described above, the CaO soil improver was certified in 2014 as a safe, useful technology for improving the environment of sea areas.

3.2 Evaluation of other biological effects

In many cases, the degree of contamination of sediments in a sea area is judged by the contents and amounts of elution of harmful substances. In this connection, a proposal has been made to evaluate not only those chemical properties of sediments but also their toxicity to living things.[18] From the standpoint of environmental impacts, it has been recommended that for the species making up the ecosystems, as well as the useful marine bio-resources mentioned above, several representative living things selected by hierarchical level

Table 2 Example of results of acute toxicity tests

Concentration of test solution (%)	Iron supply unit			Slag rock/block		
	Fish	Shellfish	Prawn	Fish	Shellfish	Prawn
0	0% (0/10)	0% (0/10)	0% (0/20)	0% (0/10)	0% (0/10)	0% (0/20)
25	0% (0/10)	0% (0/10)	0% (0/20)	0% (0/10)	0% (0/10)	0% (0/20)
50	10% (1*/10)	0% (0/10)	0% (0/20)	0% (0/10)	0% (0/10)	0% (0/20)
75	0% (0/10)	0% (0/10)	0% (0/20)	0% (0/10)	0% (0/10)	0% (0/20)
100	0% (0/10)	0% (0/10)	0% (0/20)	0% (0/10)	0% (0/10)	0% (0/20)

* Falling dead by the struggle between the individual.

with consideration given to the food chain be subjected to a toxicity test. Although standard test methods for various species living in freshwater have been proposed, practical test methods for marine life have yet to be developed.

Under the guidance of Takashi Kusui, professor at Toyama Prefectural University, we discussed biological toxicity tests using marine life and made an attempt to evaluate the effect of steelmaking slag on marine life. So far, they have studied phytoplankton—the primary producers, animal plankton preying upon them, higher-order shells and sea urchins, and bacteria, which are the decomposers. Presented below are examples of evaluation of the eluate of steelmaking slag using light-emitting sea bacteria (Vibrio fischeri for testing the inhibition of light emission) and water fleas (Tigriopus japonicas for testing the inhibition of floating activity).[19)]

In each of the above tests, an eluate of steelmaking slag prepared by the tank leaching method using artificial seawater as the solvent was evaluated. As a result, it was found that the inhibiting reaction was conspicuous when the eluate had a large pH value. When the eluate of large pH value was neutralized to the level of pH of seawater (pH = 8), the emission of light from Vibrio fischeri somewhat increased, rather than becoming inhibited, whereas the floating action of Tigriopus japonicas remained inhibited. This was found due to a rise in Ca concentration of the seawater caused by Ca eluted from the slag. Namely, in the above biological tests, it was concluded that the test results were influenced by the change in pH of seawater and the resulting change in hardness of seawater, specifically the change in Ca concentration of seawater: the effects of harmful substances were not observed at all. Reportedly, the change in pH value of seawater under ordinary conditions of application of slag is negligibly small.[20)] Then, it may be said that the influence of high pH observed in the above biological tests can be left out of consideration.

4. Conclusion

In utilizing steelmaking slag as a basic material for fisheries, it is considered necessary not only to demonstrate the usefulness of slag but also to continue accumulating as much data as possible about the safety of slag used in the environment of sea areas.

In 2011, with the aim of assessing the long-term environmental impact of using steelmaking slag in sea areas, Nippon Steel & Sumitomo Metal constructed “SeaLabo II,” which has made it possible to accumulate relevant experimental data throughout the year. At present, the effect of steelmaking slag on the growth of Japanese littlenecks is being studied at SeaLabo II.

In order to allow for extensive application of our steelmaking slag products and make them widely accepted by society, we intend to expand our technology development for creating an environment in which the slag products can be used safely, through studies at various stages from basic experiments in the laboratory to verification experiments in diverse sea areas giving consideration to what is really needed.

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