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Application of Steelmaking Slag to Marine Forest Restoration

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Abstract

Steelmaking slag is a valuable material, which can be used as fertilizer or artificial rock, also in the coastal area as well as on the land. First, we focus on ferrous ion, which is the essential element in seaweed growth, from the slag. We carry out the fundamental experiments from laboratory scale to actual field scale to demonstrate the efficacy of slag as ferrous fertilizer. Second, we propose the usage of slag stone for seaweed bed basement and succeed in seaweed growing on the surface of slag stone in several field tests. We continue to evaluate the efficacy and safeness of the steelmaking slag when using it in marine.

1. Introduction

In Japan's coastal regions, we have come to witness a frequently occurring phenomenon called sea desertification whereby communities of large seaweeds, which afford places of spawning and growing of fishes disappear, causing problems such as the decline in fish catches.

It is considered that sea desertification occurs because of the combination of various factors, including the rise of seawater temperature, the deterioration of water quality caused largely by industrial development activities, the excessive eating pressure of sea urchins and many species of fishes, etc. To prevent this undesirable phenomenon, various measures have been taken—putting an adhesion base into the sea, which helps reduce the eating pressure on the seaweed communities, directly exterminating the harmful animals, etc. Conversely, it has been noticed that in certain sea areas, sea desertification may be ascribable to excessively low concentrations of nutrient salts and iron that are indispensable for the growth of seaweeds.

Steelmaking slag contains considerable proportions of iron (II) and silicon, which are necessary for the sound growth of seaweeds. Therefore, it is possible to utilize steelmaking slag as a source of nutrient salt or substrate for restoring seaweed grounds in an oligotrophic coastal area if the elution of alkalis from the slag can be restrained effectively.

In recent years, increasing attention has been paid to the supply of nutrients from forests to the sea via rivers. In addition, it is said that forests have become an important source of nutrient salts and iron. The type of iron required for the growth of seaweeds is called as iron (II), i.e., iron dissolved in water. This type of iron is immediately oxidized into iron (III) by the oxygen dissolved in seawater and it precipitates in the form of colloidal hydroxide. On the other hand, in forest soil, iron (II) is stable against oxidation as it forms a complex with humic acid. It is considered that iron (II) is then supplied to the seaweeds via river water.

"Vivary™ Unit" developed by Nippon Steel & Sumitomo Metal Corporation is a material useful for the restoration of damaged seaweed grounds. It is a mixture of steelmaking slag containing high contents of iron (II) and artificial humus soil produced by the fermentation of waste wood chips. This material supplies iron to the sea area, thereby helping to restore damaged seaweed grounds. Since the product was applied for the first time in a series of experiments in an actual sea area at Mashike Town in Hokkaido in October 2004, it has been used in about 30 sea areas throughout the country. In the meantime, knowledge about the safety and usefulness of the product has been accumulated. In July 2010, the product was approved as a technology useful product for the restoration of fishing grounds by the steelmaking slag product safety confirmation and certification system of the Japan Fisheries Science and Technology Association on behalf of the Japan Fisheries Cooperatives.

In addition, the company came up with an artificial mineral that supplies iron, phosphorus, and other nutrient salts. The safety and effectiveness of the product were verified in the FY 2012 Environmental Technology Verification Project (ETV Project) of the Ministry of Environment. The company also developed substrates to facilitate the settlement of seaweeds. They include Vivary™ Block and Vivary™ Rock, which are a block and stone, respectively, manufactured by hydration and consolidation of a fine powder of blast furnace slag in the form of concrete utilizing the alkali stimulus of

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steelmaking slag. Like Vivary™ Unit, Vivary™ Block and Vivary™ Rock were approved as technologies useful for the restoration of fishing grounds by the steelmaking slag product safety confirmation and certification system of the Japan Fisheries Science and Technology Association.

In this report, we shall describe the safety and usefulness of our steelmaking slag products developed for the restoration of seaweed grounds, along with some examples of their applications.

2. Discussions on Action Mechanism and Safety of Iron Feeding Technology

2.1 Effect of iron on growth of seaweeds

Seaweeds have a lifecycle in which the generation of sporophyte and the generation of gametophyte are repeated alternately. For example, in the case of *Laminaria religiosa*, the lifecycle as shown in **Fig. 1** [1] is completed in one year. The "kelp," which is familiar to us as a seaweed food, is a sporophyte reaching several meters in length. The sporophyte discharges zoospores produced by meiosis. After all the zoospores settle onto a substratum, they form microscopic male and female gametophytes in the form of single threads. Under suitable conditions, the male and female gametophytes ripe into sperms and eggs, respectively, which are fertilized to generate sporophytes. Thus, if the transition from one stage to another is impeded along the way, the new kelp is not reproduced. Motomura et al.[2] found that iron is indispensable for the ripening of gametophytes of *Laminaria religiosa*. We started the study by reconfirming the above finding.

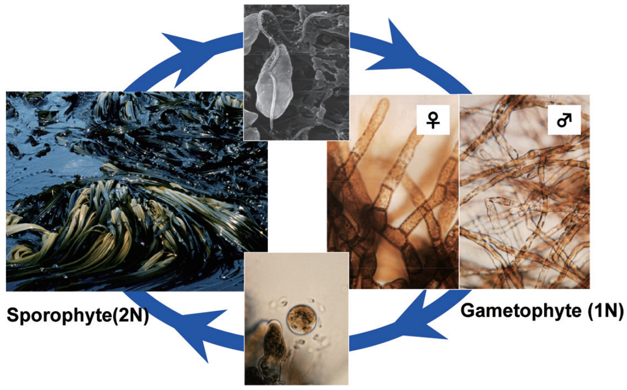

Fig. 1 Lifecycle of *Laminaria religiosa*

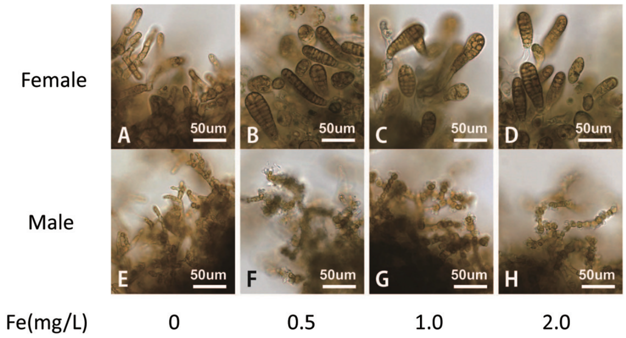

Fig. 2 Effect of ferrous ion on oogoniumu formation of *Laminaria religiosa* female and male gametophytes
Female (A-D) or male (E-H) gametophytes were incubated in Fe-free ASP12NTA medium supplemented with 0 mg/L (A,E), 0.5 mg/L (B,F), 1 mg/L (C,G), or 2 mg/L (D,H) as Fe for three weeks at 10°C.

Using the male and female gametophytes obtained by the isolation culture of zoospores of *Laminaria religiosa* collected from the coast of Mashike Town in Hokkaido, we performed an experiment on the supply of iron ions with the artificially-synthesized ASP12NTA medium as the basic medium. Consequently, it was found that in the ASP12NTA medium not containing iron, the male and female gametophytes showed vegetative growth in the form of a filamentous shape, but in the medium containing iron (0.5 mg/L, 1 mg/L, 2 mg/L), the female and male gametophyte began forming an archegonium and antheridium, respectively, each discharging eggs and sperms, and the fertilized eggs grew into sporophytes (**Fig. 2**). From these results, we confirm that iron is indispensable for the ripening of *Laminaria religiosa* gametophytes. In our subsequent study, we performed a similar culture experiment using a humic acid solution extracted from Vivary™ Unit. As a result, it was confirmed that the solution was effective for the ripening of male and female gametophytes and the growth of *Laminaria religiosa* sporophytes.[3]

It has also been confirmed that iron not only helps with the growth of seaweeds but also enhances the quality thereof. For example, concerning the discolouration of laver, which was formerly considered a problem of quality deterioration caused by a deficiency of nitrogen and/or phosphorus, it has been shown that the undesirable phenomenon can occur as a result of iron deficiency even when there are sufficient amounts of nitrogen and phosphorus.[4]

In view of the difficulty in verifying the effect of iron on the growth of seaweeds in an actual sea area, we performed a water tank experiment using deep ocean water obtained from Toyama Bay (Nyuzenmachi, Toyama prefecture), whose iron concentration is relatively low and stable.[5] The deep ocean water was led into an indoor water tank (capacity: 100 L) and Laminaria japonica was cultured in batches for studying the difference made by the input of Vivary™ Unit as fertilizer. As a result, it was confirmed that iron and other nutrient salts were eluted from the fertilizer. Further, the germination density of sporophyte of Laminaria japonica was high; and the leaf body color became more vivid.

Pyropia yezoensis was test-cultivated in large-scale water tanks ("SEALABO") installed in the RE Center of Nippon Steel & Sumitomo Metal.[6] The seawater used was led in from Tokyo Bay. One of the two FRP tanks (inside dimensions: 1 m (W) × 5 m (D) × 1.6 m (H)) was added with Vivary™ Unit and used as the experimental zone, and the other tank without Vivary™ Unit was used as the reference zone. In the experiment, the change in quality of the seawater and the condition of growth of Pyropia yezoensis were observed. As a result, in the experimental zone, the elution of nitrogen, phosphorus, silicon, and iron was confirmed by the 10th day of experiment, whereas in the reference zone, those nutrient elements decreased slowly. On the 16th day after start of the experiment, leaf bodies of Pyropia yezoensis less than 100 μm in length could be observed in both zones. From around the 48th day, the leaf bodies in the experimental zone grew to become visible with an unaided eye (leaf length: 1–2.5 cm). In the reference zone, however, the growth of leaf bodies could not be observed. From these results, it was confirmed that the supply of nutrient salts from Vivary™ Unit was effective for promoting the growth of the laver. However, the effect of iron alone has yet to be clarified by the water tank test.

2.2 Discussion on iron elution from Vivary™ unit

The amount of iron eluted from Vivary™ Unit can be quantitatively evaluated by the water tank experiment described above.

Table 1 Results of Fe elution rate from slag fertilizer

Elution condition	Elution test type	Elution rate (mg-Fe/kg-unit/d)	Relative value
Static	Small water tank	0.14	1
Static	Big water tank	0.20	1.4
Flow-through	Colum elution	0.70	5.0
Strong stirring	Bottle shaking	7.0	50

However, since it can be easily expected that the amount of iron elution varies according to physical conditions of the sea (e.g., the pounding of waves), we made a quantitative comparison of iron elution under several different conditions.

The results are shown in **Table 1**.[7] First, using carbonated steelmaking slag and artificial humus soil singly or in combination, we performed a serial batch elution experiment in which each specimen is first shaken for iron extraction in artificial seawater (Lyman & Fleming composition) for 24 hours and then the residue after centrifugal separation is re-shaken for iron extraction in the artificial seawater.[8] As a result, it was confirmed that with the slag alone, the amount of elution of iron was small in the early stages; moreover, with the mixture of slag and humus soil, the amount of iron elution increased, although the humus soil alone eluted a certain amount of iron. The rate of iron elution when the seawater was strongly stirred was 7.0 mg/kg/d.

In another experiment wherein artificial seawater was passed through a cylinder filled with a similar mixture from above, the rate of iron elution was 0.7 mg/kg/d. In yet another experiment using the SEALABO water tank mentioned earlier, the iron elution rate was 0.20 mg/kg/d. When the specimen was spread over the bottom of the water tank, the rate of iron elusion became 0.14 mg/kg/d. Thus, it was found that iron elution from Vivary™ Unit varies about 50 times depending on the physical environment under which the unit is placed.

Using a mixture of slag and humus soil, Yamamoto et al.[9] also performed an elution test in flowing water and reported an iron elution rate of 0.76 mg/kg/d, which is close to the value we obtained in our column test shown in Table 1.

We established a method of analyzing extremely small amounts of iron contained in seawater in coastal areas[10] and conducted an iron analysis in the sea area for experimental restoration of lost seaweed grounds at Mashike Town in Hokkaido described later. The dispersion of iron from the points of installation of the fertilizer units (Vivary™ Unit) toward the offing was observed. The iron content of seawater was 18 μg/L 3 m away from the water's edge nearest to the point of fertilizer installation. It gradually decreased toward the offing. It was 2.6 μg/L at a distance of 50 m in the offing, the average iron content being 4.8 μg/L.[11] The sea area under consideration is shallow for some distance from the shore, about 1.5 m in depth at a point 50 m in the offing. Assuming that iron was eluted at the above-mentioned rate (0.7 mg/kg/d) for 24 hours, it is estimated that 4.2 grams of iron was eluted from the 6 tons of fertilizer units installed in the sea. On the assumption that iron contained in the fertilizer units was dispersed in the seawater volume (975 m^3) (installation width of 26 m up to 50 m in the offing), the average iron concentration was estimated to be 4.3 μg/L.[12] As the estimated iron concentration agrees well with the average of observed values, we consider that we could determine the rate of iron elution from Vivary™ Unit with fair accuracy.

2.3 Evaluation of safety

In the process of certification of the safety of the Vivary™ Series (Unit, Rock, Block)—products for the restoration of damaged seaweed grounds—by the steelmaking slag product safety confirmation & certification system of the National Federation of Fisheries Cooperative Associations, it was confirmed that the Vivary™ Series has no acute toxicity against marine products, including the red sea bream, black abalone, and prawn. In addition, we implement quality control to ensure that the Vivary™ Series elutes no harmful substances on the basis of the criteria for seabed sediments in the Law on the Prevention of Marine Pollution and Maritime Disaster ("Marine Pollution Prevention Law"). Furthermore, we regularly examine samples of seawater and marine products collected from the sites of restoration work to see if there is elution of heavy metals or unusual concentration of harmful substances.

With the aim of strongly supporting the activity to verify the safety of the Vivary™ Series in actual sea areas that are subject to wide fluctuations of meteorological and oceanographic conditions, Nippon Steel & Sumitomo Metal opened the ocean environment simulation facility "SeaLabo-I" in 2009 and has been striving to obtain objective data about the usefulness and safety of the Vivary™ Series since then.[1] In 2011, the company installed "SeaLabo-II" to assess the long-term impact of the Vivary™ Series on the sea environment.[13]

3. Examples of Application in Restoration of Seaweed Grounds

3.1 Example of application of Vivary™ Unit

Ten years have passed since the first attempt to restore seaweed grounds using Vivary™ Unit was started at Shakuma Coast of Mashike Town, Hokkaido in 2004.[12, 14–16] So far, the quality of water, the condition of growth of seaweeds, etc. have been investigated on a regular basis. As shown in **Fig. 3**, the rate of growth of *Laminaria religiosa*, which is the principal seaweed in the sea area under consideration, has been generally higher in the experimental zone than in the control zone, although there are fluctuations from year to year. With respect to the dissolved Fe concentration of seawater that was analyzed since 2007 when the method of measurement was established,[17] it has been confirmed that the experimental zone showed higher concentrations for five years after installation of the Vivary™ Unit (**Fig. 4**). Even in the sixth and subsequent years during which the difference in dissolved Fe concentration between the two zones is not very conspicuous, the seaweeds have continued flourishing (**Photo 1**), suggesting that the vegetation that has grown thus far is functioning as a nuclear seaweed ground.

3.2 Example of application of artificial mineral

An experiment was performed to verify the effect on the growth

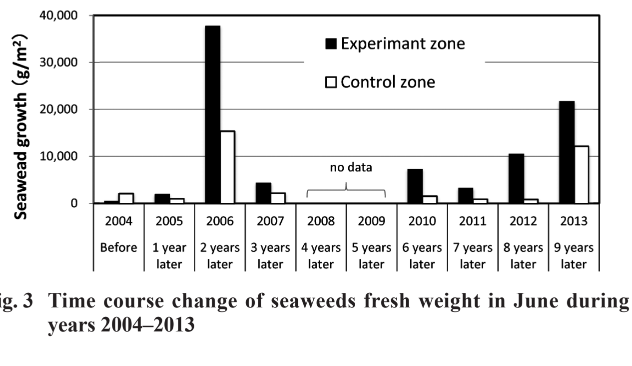

Fig. 3 Time course change of seaweeds fresh weight in June during years 2004–2013

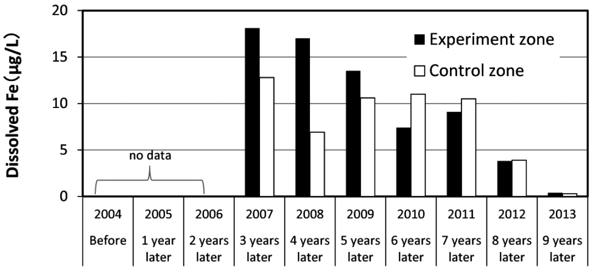

Fig. 4 Time course change of dissolved Fe concentration in seawater in June during years 2007–2013

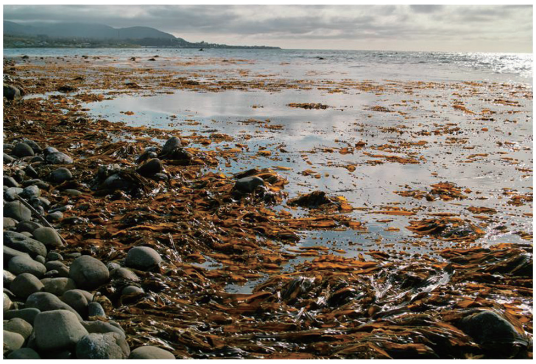

Photo 1 Photograph of experimental field in Mashike town on June in 2013

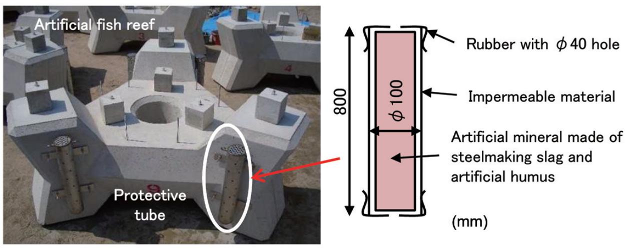

Fig. 5 Artificial fish reef and artificial mineral unit

of Ecklonia cava of artificial mineral Type M that is a mixture of steelmaking slag and artificial humus soil developed for restoration of damaged ecosystems of a sea area.[18)]

Figure 5 shows the structure of artificial mineral Type M. Steelmaking slag is mixed with humus soil to retain the minerals eluted from the slag. The mixture is put in a case made of impermeable material and each end of the case is provided with a rubber cover with a small hole in it to permit adjusting the amount of inflow of seawater. Each artificial mineral unit was put in a protective case fitted to an artificial reef block and sunk in the sea area.

The above verification experiment was performed in 2012 in the field of water environment improvement technology for closed sea areas as part of the Environmental Technology Verification Project of the Ministry of Environment. The artificial reef blocks were sunk in sandy soil about 10 m in depth of water of Kanzakiura, Minamiisecho, Watarai-gun, Mie prefecture. The number of artificial mineral units installed was six in test field No. 1 and three in test field No. 2 (none in the control field). In each of the fields, four artificial reef blocks were sunk and the number and length of sporophytes of Ecklonia cava settled were measured (**Fig. 6**, **Table 2**).

Figure 7 shows the results obtained six months after the blocks were sunk. The settlement of sporophytes of Ecklonia cava was observed in each field. It was confirmed, however, that the number and length of sporophytes of Ecklonia cava settled differ according to the number of artificial mineral units installed in artificial reef blocks. **Figure 8** shows the condition of growth of sporophytes in each of the fields 10 months after the artificial reef block was sunk. It was confirmed that the condition of growth was better in test field 1 than in test field 2.

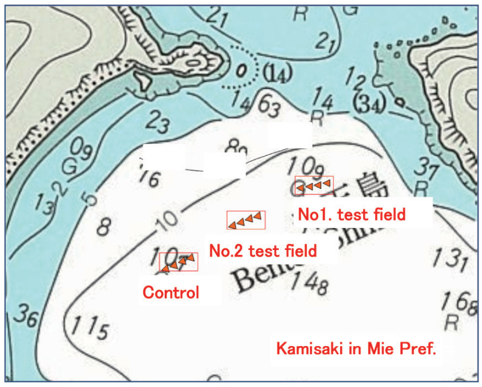

Fig. 6 Map of test fields

Table 2 Number of installed block and units

	Control	Test field	
		No. 2	No. 1
Artificial fish reef (block)	4	4	4
Artificial mineral (unit/block)	0	3	6

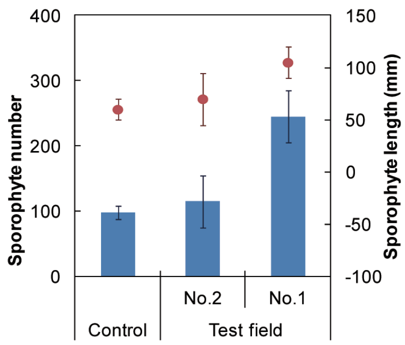

Fig. 7 Comparison of sporophyte number and length

3.3 Example of application of Vivary™ Rock

For a sandy ground where there is no base on which seaweeds could be settled, the company proposes using its hydrated steelmaking slag product (Vivary™ Rock)[19)] as a material for the mound. In the sea area of Iki, Nagasaki prefecture, an artificial algae reef (**Fig. 9**) was installed in 2010. Vivary™ Unit (steel box type) was installed at the center of the reef with the expectation that it would help create a seaweed ground in the sea area by supplying iron. In the summer of 2013, the luxuriant growth of Eisenia bicyclis and Ecklonia cava as shown in **Photo 2** was confirmed. In addition, iron (II) was detected only right above the Unit.[20)] The fact that iron (II), which is said to have high bioavailability, was observed in the

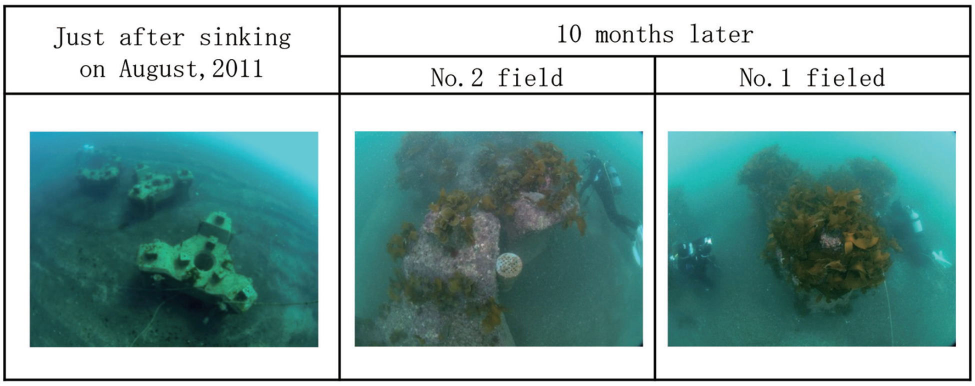

Fig. 8 10 months later after sinking artificial fish leaf with artificial mineral

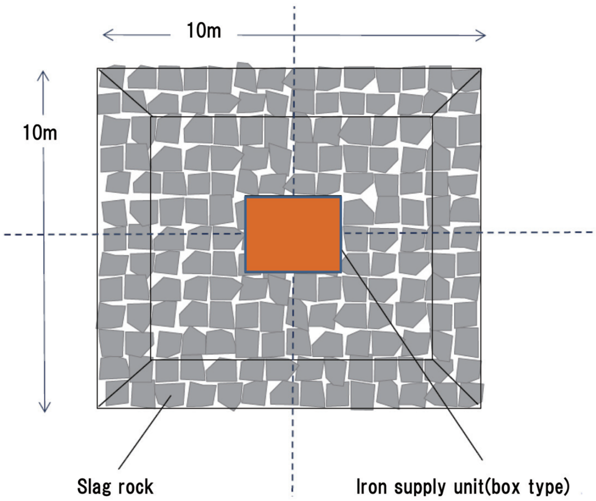

Fig. 9 Diagram of the breeding ground for seaweed

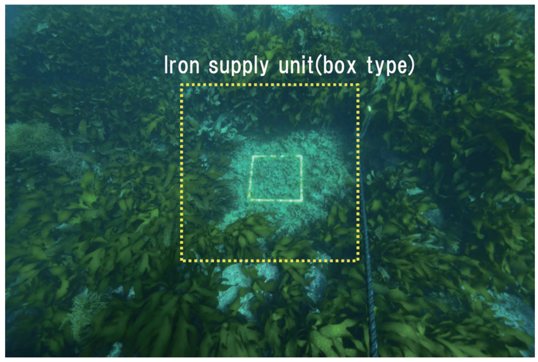

Photo 2 Photograph of experimental field in Iki Island on July in 2013

neighborhood of the Vivary™ Unit and is very meaningful. It is hoped that the correlation between iron supply and seaweed growth will be studied in the future.

4. Conclusion

In order to restore coastal algae grounds that have been damaged or lost due to sea desertification, we consider it important to investigate the cause and take every necessary measure. Using steelmaking slag to supply iron to those grounds is just one of the many conceivable measures. Even so, it is considered necessary to verify the effect of supplying iron, identify the sea areas that really need iron supply, and determine the conditions for iron supply.

Restoring algae grounds in coastal areas not only helps activate the coastal fisheries but is also important from the standpoint of blue carbon, which assumes the oceans as a great absorber of carbon dioxide.[21] We intend to develop and offer new technologies that contribute to the improvement of the ocean environment of Japan as a seafaring nation.

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