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Sea Forest Creation Utilizing By-Product Slag of Steelmaking Process (Development of Technology for Regeneration of Seaweed Bed)

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1. Introduction

Japan is an island nation surrounded by sea. It has a total coastline of some 35,000 km, ranked sixth in the world. Today, quite a few of its coastal areas that were formerly prosperous coastal fisheries are suffering from a phenomenon called sea desertification,[1] whereby useful seaweed such as kelp and gulfweed are prevented from growing. Sea desertification has been a heavy blow to coastal fisheries in those areas since it has led to a remarkable decrease not only in the production of seaweed, but also in fisheries. Sea desertification is thought to be caused by various factors, including a rise in seawater temperature and the resulting change in ocean currents, as well as excessive feeding by sea urchins, fish and shellfish, etc. In order to safeguard marine resources, various measures have been devised and numerous demonstration tests on creating seaweed beds have been conducted.[2-4]

On the other hand, a change in the nutritional composition of the sea in those areas, specifically a decline in concentration of iron,[5] a trace element indispensable for seaweed growth, was suggested as another factor in the occurrence and spread of sea desertification.[6-7] In response to the above suggestion, attempts have been made to foster a seaweed bed by supplying an appropriate amount of iron to the locality.[8-9] When iron is supplied to the sea, bivalent iron is immediately oxidized into trivalent iron by oxygen dissolved in the seawater and precipitates in the seawater in the form of an insoluble hydroxide.[10] Since this markedly decreases the biological utility of iron, it is important to ensure a stable supply of iron in the form of dissolved iron.

From the standpoint of supplying the marine locality with dissolved iron on a stable basis, Nippon Steel Corporation has created a fertilizer composed of humus soil and iron sources with an eye on providing “humic acid (fulvic acid) iron—a complex of iron ions” that naturally exists in humus in the soil and that is carried into the locality by rivers, etc. Of the by-products of the steelmaking process, converter slag contains a high concentration of bivalent iron (FeO). This slag, used as the source of iron, is mixed with artificial humus in the soil obtained by fermenting chips of waste wood to produce the above fertilizer for creating seaweed beds. The fertilizer has been put on the market under the product name “Beverly®Unit.” Experiments using the fertilizer to create a seaweed bed composed of kelp mainly in a sea area by supplying iron to a sea desert zone on a stable basis were first carried out in Hokkaido on the Japan Sea coast. These efforts have produced tangible results in terms of the regeneration of seaweed beds.[11-12]

In particular, at Mashike Town in Hokkaido, the Mashike Fisheries Cooperative had been active in its efforts to regenerate seaweed beds in a sea desert zone using a fertilizer made from fishmeal. Since October 2004, in conjunction with the above fisheries cooperative, we have studied the effect of Beverly® Unit embedded in a badly affected area of sea desert over 26 m along the Shakuma Coast shoreline. During our study carried out in June 2005, we found that kelp and other seaweeds had already flourished in the experimental sea area and that the yield of kelp per unit area there was more than 100 times that in non-fertilized areas. Today, at the Shakuma Coast, where seaweed was formerly seldom seen, barring coralline algae, which had covered the surface of the rocks at the bottom of the sea, kelp and other seaweeds are growing healthily in the experimental sea area.

Thus, along the Shakuma Coast at Mashike Town, the regeneration and expansion of a seaweed bed over a wide area has been confirmed in and around the fertilized zone.[13] At present, in light of the above achievement, about twenty coastal communities throughout the country are attempting to develop “sea forests”. For example, *Eisenia bicyclis* and *Ecklonia cava* (both edible seaweeds) are flourishing in the sea off Shima City, Mie Prefecture and gulfweeds are growing thickly in the sea off Tanabe City, Wakayama Prefecture and Himejima, Oita Prefecture. Thus, in various parts of the country, the favorable effect of supplying iron as a fertilizer for seaweeds has been demonstrated. Seaweed not only feeds fish and shellfish, but also provides them with somewhere to live and spawn. Regenerating seaweed beds which themselves nurture a variety of life forms also helps to increase marine resources. In this regard, its significance is even greater, and is not limited to just increasing the yield of seaweed.

While promoting the above activity to create seaweed beds, the authors have conducted experiments to scientifically verify the effect of applying Beverly® Unit as a fertilizer for seaweeds. At first, it was difficult to accurately measure the iron concentration of seawater in coastal areas, which contain many impurities, and therefore, we could not clarify the effect of fertilization on iron concentration in the experimental sea area.[12]

Eventually, by applying a technique developed by the Analytical

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Sciences Laboratory of the Advanced Technology Research Center of Nippon Steel to accurately measure the concentration of a miniscule amounts of iron in the seawater of coastal areas,[14] it became possible to grasp the state of the iron eluted from the fertilizer as it was dispersed over a wide area.[15] In addition, it has been clarified through cultivation experiments conducted in a laboratory that iron plays an important role in the growth and life cycle of seaweeds. Therefore, we undertook various studies on the influence of iron on seaweeds and attempted to verify the study results in the laboratory. Examples of the verification results are given below.

2. Verification of Effects of Iron on Seaweed (Kelp Plants [Laminariales])

2.1 Verification of influence of iron on maturation of gametophytes of *Saccharia japonica* var. *religiosa*

Fig. 1 shows the life cycle of Laminariales plants. It can be seen from the figure that the familiar "kelp" several meters in length is a sporophyte. From the sporophyte, zoospores are released through meiosis. After those zoospores attach to a substrate, they germinate tiny male or female gametophytes in the form of a single string. The male and female gametophytes mature under suitable conditions to produce eggs or sperm for fertilization. Each fertilized egg eventually grows into a sporophyte. Thus, *S. japonica* var. *religiosa* completes the above life cycle in one year. What is more important than anything else here is that new "kelp" is not born if the transition from one stage to the next in the life cycle fails for some reason. In the present experiment, with an eye on the Laminariales life cycle, we studied the influence of iron on the maturation of male and female gametophytes, which is the production of eggs and sperm, using various types of iron compounds.

The samples used are male and female gametophytes obtained by culturing zoospores in isolation from *S. japonica* var. *religiosa* collected at Mashike in Hokkaido in November 2009. Those samples had been subjected to sterile culture at the Muroran Marine Station, Field Science Center for Northern Biosphere at Hokkaido University.

First, we prepared a fulvic acid solution from the fertilizer for seaweed bed creation (Beverly® Unit)—a mixture of converter slag (steelmaking slag) containing a large proportion of iron and artificial humus made by fermenting waste wood chips.[16] Then, we studied the maturation of male and female gametophytes using, as the medium, Fe-free $ASP_{12}NTA$ (artificial seawater containing large proportions of nonferrous nutrients) with the fulvic acid solution added to adjust the Fe concentration of the medium to between 0.2 μg/L and 0.1 mg/L (**Fig. 2**).

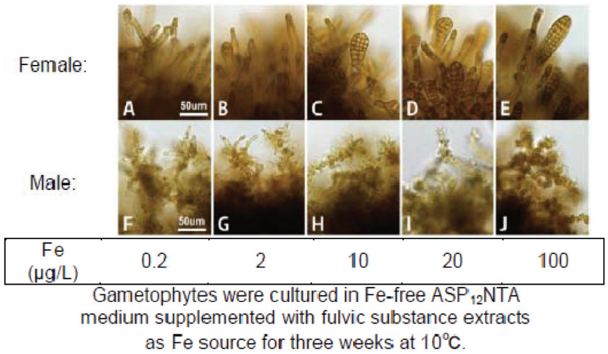

Fig. 2 Effect of fulvic substances on female and male of *S. japonica* var. *religiosa* gametophytes

In the Fe-free $ASP_{12}NTA$ medium containing 10 μg/L or more of Fe, the male and female gametophytes of *S. japonica* var. *religiosa* grew markedly and the eggs were fertilized by the sperm to become sporophytes. From these results, we could confirm that like natural humus substances, the slag-based fertilizer contained some element that can promote the maturation of male and female gametophytes of Laminariales. In view of the fact that the medium used in the present experiment contained excessively large proportions of nitrogen and phosphorus, it is considered very likely that the element that can really promote the maturation of male and female gametophytes of *S. japonica* var. *religiosa* is seawater-soluble iron like fulvic acid iron.[17-19]

2.2 Verification of iron's effect on sporophytes of *S. japonica* var. *religiosa*[20]

We cultured immature sporophytes of *S. japonica* var. *religiosa* in a Fe-free $ASP_{12}NTA$ medium with and without the addition of 0.3 - 3 mg/L of fulvic substance extract (2.9 - 29 μg/L in terms of Fe concentration) at 10℃ for three weeks under long-day conditions to observe the growth of those sporophytes. The fulvic substance extract (fulvic acid iron) was obtained as follows. First, a mixture of 50 grams of carbonized steelmaking slag and 50 grams of artificial humus was shake-extracted in 1 liter of pure water for 24 hours and subjected to centrifugal separation to recover the supernatant, which had hydrochloric acid added until its pH value became 1. Next, the solution was stirred for 24 hours and then subjected to centrifugal separation to obtain the supernatant (acid-soluble component), which was frozen and dried.

The fulvic substance extract used in the culture experiment contained 0.97% Fe, 1.03% N and 0.78% P (w/w). In the experiment, a solution of Fe-free $ASP_{12}NTA$ medium in which 300 mg/L of fulvic substance extract was dissolved (measured Fe concentration = 2.9 mg/L) was diluted 100 to 1,000 times with Fe-free $ASP_{12}NTA$ medium. Since the Fe-free $ASP_{12}NTA$ medium contained 2.4 μg/L of iron (measured value) as the background, the Fe concentrations of the two media used were calculated as 31.4 μg/L and 5.3 μg/L, respectively.

As shown in **Fig. 3**, after three weeks, the sporophytes in the Fe-free $ASP_{12}NTA$ medium (C) grew very little, whereas those in media with fulvic acid iron added (A, B) grew markedly. The implication is that fulvic acid iron of even several μg/L in terms of Fe concentration is likely to help promote the growth of sporophytes of *S. japonica*

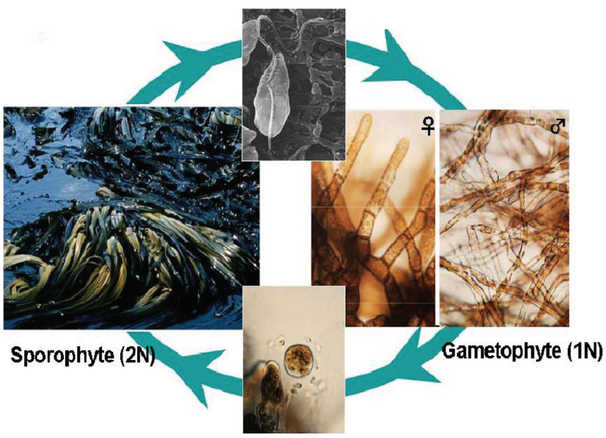

Fig. 1 Life cycle of Laminariales

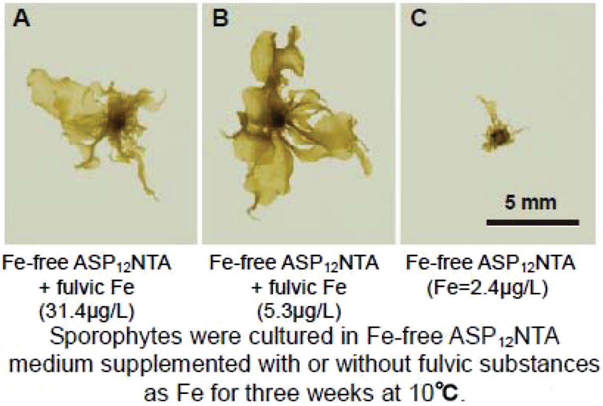

Fig. 3 Effect of fulvic substances on growth of *S. japonica* var. *religiosa* sporophytes

var. *religiosa*. According to Motomura et al.[21)], Fe is indispensable for the maturation of gametophytes of *S. angustata*. They report that when EDTA-Fe (II) with an Fe concentration of 0.5 mg/L or more was used, they could observe the maturation of gametophytes. Although their findings cannot strictly be compared with the results shown in Fig. 3 because of the difference in the evaluation system used, it may well be estimated that fulvic acid iron has higher biological activity than artificial chelated iron (EDTA-Fe (II)) even when the Fe concentration is lower.

3. Future Activity

In order to scientifically clarify the utility and safety of steelmaking slag, Nippon Steel opened a facility to simulate the marine environment (“SEA-Lab.”) within the Technology Development Center in Futtsu City, Chiba in April 2009 (**Photo 1**).

In the SEA-Lab., which is equipped with water tanks simulating seaweed beds and shoals, Nippon Steel has carried out various simulative tests on the marine environment of coastal areas and the regeneration of seaweed beds. So far, the company has demonstrated the effect of applying its slag-based fertilizer on the growth and color of *Pyropia yezoensis* (laver). In addition, various studies on the utility and safety of other slag-based products have been conducted.[22)]

Under those conditions, “Beverly® Unit” and “Beverly® Block/ Beverly® Rock”—Nippon Steel’s two products for development of seaweed beds—was awarded a safety certification by the Steel Slag-based Product Safety Confirmation and Certification System that has been newly established by the National Federation of Fisheries Co-operative Associations. The safety certification confirms that in acute toxicity tests on red sea bream, black abalone and prawns, there were no deaths caused by application of the fertilizer. It also clearly states standards for quality control of the above products. Nippon Steel considers that the high degree of safety of its fertilizers has been guaranteed.

Photo 1 Appearance of new facility called “SEA-Lab.”

On the other hand, the activity to create “sea forests” has been attracting attention as a measure to curb global warming. In August 2009, the “Model Project to Demonstrate CO_2 Absorption by Seaweed in Subarctic Coastal Areas Utilizing Recyclable Agricultural & Industrial Resources” was adopted as one of the “Model Projects for Technology Discovery/Social System Demonstration for the Materialization of a Low-Carbon Society” of the Hokkaido Bureau of Economy, Trade and Industry under the Ministry of Economy, Trade and Industry. Aiming to demonstrate the absorption of CO_2 through the creation of “sea forests”, the above project is to be carried out jointly by Nippon Steel, Nippon Steel Chemical, Econix, Tetsugen Corporation, Penta-Ocean Construction Co., Hokkaido University and Shizuoka University, with Muroran Techno-Center as the managing corporation. A demonstration test was started in the sea off Suttu Town in Hokkaido in August 2010 and in the sea off Muroran City in October of the same year.

Specifically, the project aims to build a system consisting of these three pillars: (1) using a solid hydrate of steel slag for alga reef blocks since less CO_2 is emitted during the manufacturing process than for conventional cement blocks, (2) allowing seaweed absorbed CO_2 to grow up in the “sea forests”, and (3) processing the seaweed into resin/oil to fix the CO_2 for an extended period of time. It is estimated that the reduction in CO_2 in the above two marine areas will be 44 tons per year during the current project period. If the project is spread throughout the seas off Hokkaido (about 30,000 ha of sea forest development) in the future, the total reduction in CO_2 is estimated to reach about five million tons.

4. Conclusion

In the future, we intend to clarify which technology permits making the most effective use of our Beverly® Units and various other products made from steelmaking slag through our continued evaluation of the long-term effect of steelmaking slag on aquatic organisms, etc.

References

1) Fujita, D.: Barren Ground, In Current State of Phycology in the 21st Century, Hori, T. et al. Eds., The Japanese Society of Phycology, Yamagata, 2002, p.102
2) Harold, C. et al.: Ecology. 66 (4), 1160 (1985)
3) Kuwahara, H. et al.: Fisheries Engineering. 38 (2), 159 (2001)
4) Horie, H. et al.: J. Hokkaido For. Prod. Res. Inst. 17 (3), 1 (2003)
5) Motomura, T. et al.: Bull. Jap. Soc. Sci. Fish. 47, 1535 (1981)
6) Matsunaga, K. et al.: J. Exp. Mar. Biol. Ecol. 241, 193 (1999)
7) Suzuki, K. et al.: Phycologia. 34, 201 (1995)
8) Matsunaga, K. et al.: J. Appl. Phycol. 6, 397 (1994)
9) Matsumoto, K. et al.: J. Chem. Eng. Jpn. 39, 229 (2006)
10) Rose, A.L. et al.: Environ. Sci. Technol. 36, 433 (2002)
11) Yamamoto, M. et al.: Journal of the Japan Institute of Energy. 85, 971 (2006)
12) Kiso, H. et al.: Ecosystem Concrete for Creating Rich Coasts—Preventing Marine Desertification and Developing Sea Beds. Symposium of the Japan Society of Civil Engineers, Tokyo, 2007, p.182
13) Kiso, H. et al.: Proceedings of the 20th Ocean Engineering Symposium. Tokyo, 2008
14) Aimoto, M. et al.: Shinnittetsu Giho. (390), 89 (2010)
15) Kato, T. et al.: Proceedings of the 20th Ocean Engineering Symposium. Tokyo, 2008

16) Yamamoto, M. et al.: Bioresource Technology. 101, 4456 (2010)
17) Motomura, T. et al.: Bull. Jap. Soc. Sci. Fish. 47, 1535 (1981)
18) Motomura, T. et al.: Phycologia. 23, 331 (1984)
19) Suzuki, Y. et al.: Japan Sea Phycologia. 34, 201 (1995)
20) Kato, T. et al.: Proceedings of Lectures at the 21st Academic Lecture Meeting of the Japan Society of Fisheries Engineering. Kanagawa, 2009
21) Motomura, T. et al.: Bull. Jap. Soc. Sci. Fish. 47, 1535 (1981)
22) Ueki, C. et al.: Journal of Advanced Marine Science and Technology Society. 17, 49 (2011)

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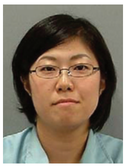

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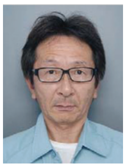

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