Technical Report

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Model Project on the CO₂ Absorption by Recyclable Resources of Agriculture-and-manufacturing in Subarctic Zone Coast

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Abstract

In Japan, the area of marine forest has decreased by 40% in the last 30 years, due to environmental changes. To develop Low-carbon society, it is inevitable to restore and expand marine forests and promote the carbon sequestration by seaweed in the coastal zone. Especially, Hokkaido, which locates in the subarctic zone, has 200000-ha marine forest which shares 20% of the domestic total. The restoration of marine forest in the coast al zone would also promote the development of industries in the area. In this project which is commissioned by Ministry of Economy, Trade and Industry, we made a unit which consists of companies, local residents, self-governing bodies and government. We conducted the experimental study to develop CO,-absorption system at marine forest which locates along the shore in subarctic zone area by using agriculture-and-manufacturing recyclable resources. The objects of this project are as follows. The first is to reduce CO, emission by using iron and steel slag instead of concrete as the material of building blocks and stones, which compose part of marine forest. The second is to enhance CO, absorption by supplying iron from the installed unit attached to the building blocks and stones which comprise marine forest, and promoting growth of seaweeds such as kombu. The last is to sequestrate carbon by manufacturing oil and resin, which could be used for industrial products, from the elements of grownup seaweed.

1. Introduction

In order to realize a low-carbon society in the seafaring Japan, it is considered necessary to restore/reconstruct seaweed grounds, which have narrowed down as much as 40% in the past 30 years due to reasons such as changes in environmental conditions, and recover the functions of seaweeds absorbing CO_2 and fixing carbon in the coastal areas. In particular, Hokkaido, which is situated in the subarctic zone, accounts for 20% of the total area of the country's seaweed grounds (200000 ha). There, promoting and activating coastal industries, etc. is strongly called for. In this context, restoring seaweed grounds in the coastal areas is extremely important. In the model project described in this report, the central and local governments, business enterprises, and local inhabitants performed a joint verification research on the absorption of CO_2 in a seaweed ground utilizing recyclable agro-engineering resources in the subarctic coastal area with the following three objectives in mind.¹⁾ 1.1 Reducing CO, emissions

In the 1000-hectare seaweed ground construction project that has been carried on in Japan since 2007, the emission of CO_2 from the cement concrete manufacturing process was estimated to be 53 000 tons a year. Under that condition, the present model project aimed to reduce the emission of CO_2 by 7.8 t- CO_2 /year by manufacturing at least 1000 m³ of hydrated steelmaking slag (hereinafter "the hydrate") in the subarctic area and substituting them for concrete since the hydrate permits reducing CO_2 emissions more easily than concrete.

1.2 Increasing CO₂ absorption

It is estimated that because of the 40% decrease in area of Japanese seaweed grounds in the last 30 years, the CO_2 absorbing capacity of seaweed grounds has declined by 7300000 tons a year. In

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view of that condition, the present model project aimed to absorb 11 tons of CO_2 a year on the Muroran and Suttsu test seaweed grounds (2000 m²) to be newly constructed by using a material composed of an iron and nutrient supply unit (hereinafter "the fertilizer unit) and the hydrate.

1.3 Fixing CO₂ for long time

It is estimated that 57% of the amount of photosynthesis of seaweeds is released into the seawater without being deposited on the seabed. If those released seaweeds are collected and made into resins, oils, and other industrial products, it can be expected that 16.2 tons of CO_2 a year will be fixed on a long-term basis in the seaweed grounds mentioned in 1.2 "Increasing CO_2 Absorption." Therefore, the present model project aimed to develop basic technology for converting seaweeds into resin or oil utilizing the subcritical water/ supercritical methanol treatment technology in the process of research and development. The results of the present model project are outlined below.

2. Main Subject

2.1 Demonstrating production of low CO₂ emission type material in subarctic region

We tackled manufacturing the hydrate as a substitute for the concrete block and stone that are commonly used in the improvement and maintenance of fisheries bases, the execution of port/seaside works, etc.

In the beginning, mixing and quality confirmation tests (examples of results of a compressive strength test are shown in **Fig. 1**) were performed to ascertain that the hydrate of steelmaking slag produced at Muroran Works meets the quality requirements and that the hydrate manufacturing process is completely workable. Since the present model project was intended for Hokkaido and other sub-arctic areas, a freeze & melt test was also performed to confirm the frost durability of the hydrate.

Next, a hydrate production plant (**Photo 1**) was constructed on the grounds of Muroran Works of Nippon Steel & Sumitomo Metal Corporation. In the equipment design, the numbers and dimensions of silos and conveyors were optimized to ensure effective mixing of the raw materials for the hydrate. After construction, the plant was test-operated to determine the optimum kneading time, etc. At the same time, it was confirmed that the hydrate manufacturing process may be the same as used in the production of ordinary concrete.

2.2 Optimizing fertilizer application and seaweed ground development in subarctic region

2.2.1 Study on effect of hydrate to promote settlement of seaweeds In the development of seaweed grounds, concrete blocks are

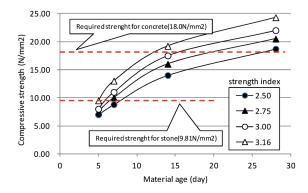


Fig. 1 Compressive strength of steel-making slag concrete (5°C curing)

generally used as objects to which seaweeds are attached. As one of its properties, however, concrete becomes alkaline when it is wetted with water. The same is true for the hydrate. With the aim of clarifying the influence of that property on the settlement of seaweeds, we studied the condition of settlement of seaweeds by a cultivation experiment using test pieces of the hydrate and concrete. As a result, it was found that in the early stages of occurrence of kelp swarm spores, the pH of seawater significantly influenced the settlement of seaweeds.

At the same time, we compared the results obtained with concrete and hydrate, respectively. When a harshness removal treatment (i.e., cleaning the test piece surface in seawater) was applied, the concrete and hydrate made no difference: the growth of many spores was observed with both types of test pieces. Without the harshness removal treatment, however, the growth of spores on the concrete surface was not observed, whereas it was observed on the hydrate surface (**Table 1**). From this test result, we consider that as a basal object in seaweed grounds, the hydrate can have a competitive edge over concrete.

2.2.2 Verification of effect of hydrate to promote settlement of seaweeds

Next, we investigated the water qualities (e.g., iron concentration), the damage to seaweeds caused by sea urchins, etc. in the Muroran and Suttsu sea areas under consideration. As a result, it was judged that the major factors limiting the growth of seaweeds were the stability of the basal object on the seabed, the quantity of light, and the concentration of iron in the Muroran sea area and the damage caused by sea urchins (water flow rate) and the concentration of iron in the Suttsu sea area. On the basis of those conditions, we performed diffusion simulations, etc. to optimize the application



Photo 1 Steel-making slag concrete plant

Table 1 Generating situation of a sea weed swarm spore

	Non-treated	Treated
Concrete	A <u>109µm</u>	
Steel-making slag concrete	100gm	

of fertilizer and the development of seaweed grounds (**Fig. 2**) and decided the arrangement, structures, etc. of seaweed reef blocks, artificial stone mounds, and iron supply units made from hydrate (**Fig. 3**).

2.2.3 Manufacturing of seaweed reef blocks and fertilizer units

On the basis of the results of the mixing and quality confirmation tests mentioned earlier, we manufactured blocks ("Alga Rock": 1.503 m³/unit) and artificial stones by mixing the raw materials and consolidating the mixtures using the hydrate plant within Muroran Works (**Photo 2**). The actual production volume was 1348 m³, much larger than the originally planned volume of 1000 m³. Those hydrate products, together with fertilizer units, were transported on trucks and barges to the sea areas and installed in the sea. The installation work was executed in October 2010 in the Muroran sea area and in August 2010 in the Suttsu sea area (**Photos 3** and **4**). 2.2.4 Evaluation of effect of seaweed ground development

About two months after installation of the seaweed reef blocks, seawater was collected from each of the sea areas and its qualities were analyzed. As a result, the elution of dissolved iron was ob-

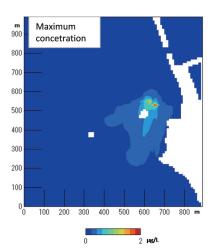


Fig. 2 Example of the simulation result of iron concentration (Muroran)

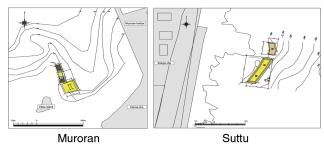


Fig. 3 Arrangement of seaweed bed



Photo 2 Steel-making slag concrete

served around the fertilizer units, indicating that iron had been supplied to the seaweed reefs (Fig. 4).

In addition, in February, four to six months after installation of the seaweed reef blocks and artificial stones, an undersea investigation of seaweeds was performed. As a result, it was found that kelps had settled on both the hydrate blocks and artificial stone mounds (**Photo 5**). There, the total standing crop of kelps grown in the con-



Photo 3 Setting of seaweed bed





Photo 4 Seaweed bed

Unit of iron-supply

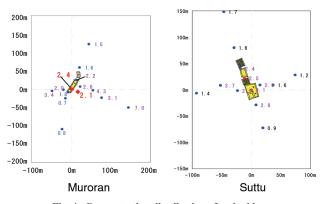


Fig. 4 Concentration distribution of melted iron





Suttu

Photo 5 Sea weed on seagrass bed

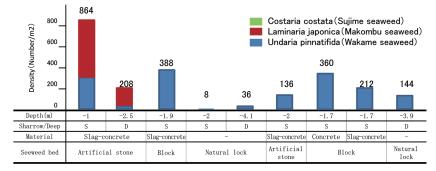


Fig. 5 Standing stock of a sea weed (Muroran)

structed seaweed reefs was estimated as the effect of the seaweed reefs on fisheries production (**Fig. 5**). In estimating the standing crop, the kelp density obtained by a preliminary investigation in each of the Muroran and Suttsu seaweed reefs was used. February and March, during which the investigation was made, are the period of early growth of kelps. Therefore, the number of kelps that actually settled in each seaweed reef was multiplied by the leaf weight (i.e., the weight per kelp) during the season to estimate the standing crop of kelps for the season. The actual standing crop of kelps in February–March was 0.077 kg-wet/m² in Muroran and 0.011 kg-wet/m² in Suttsu, and the estimated standing crop for summer was 30.5 kg-wet/m² in Muroran and 13.8 kg-wet/m² in Suttsu.

2.3 Long-term fixation of CO₂ by seaweeds converted into oil or resin

2.3.1 R&D on conversion of seaweeds into resin/oil

The seaweeds reproduced by the above activities will not only help improve the environment of sea areas and promote/activate the industries in coastal areas. They will also bring about several favorable effects. For example, if seaweeds can be made into oil and substituted for fossil fuels, it will help reduce the consumption of petroleum and the emission of CO_2 from burning petroleum products. In recent years, attempts have been made to utilize the biomass in earnest. The seas account for as much as 71% of the earth's surface area. However, few technologies have been developed to permit utilizing as a source of carbon the biomass of seaweeds, which flourish even in cold regions, and to manufacture diverse industrial products, including resins made from seaweeds, which help fix CO_2 . In this context, this project is considered meaningful. 2.3.2 Results of the present study

The biomass that exists on the earth has a relatively simple, common structure including lignin, cellulose, and hemicellulose. On the other hand, the algae biomass consists of many different types of saccharides and even algae of the same species differ in composition according to where and when they are collected. Therefore, in the present study, only two common specifies—kelp and green alga were considered.

In the study on conversion of algae into oil, it was found that the yield of oil could be maximized by increasing the quantity of sample subjected to the treatment in subcritical water and by treating the sample at a high temperature and in a short time (Fig. 6).

In the study on conversion of algae into resin, an attempt was made to produce bio-resin efficiently by means of direct polymer conversion of polysaccharides, which are the main constituent element of algae without the decomposition, fermentation, and polymerization processes (**Fig. 7**). With cellulose selected as the model polysaccharide, it was subjected to methylation using various types of acid catalysts and solid acid catalysts. In the present experimentation, the methylation of cellulose did not progress. However, we consider it possible to obtain the desired bio-resin using a much stronger solid acid or substituting alginic acid, etc. for cellulose.

2.3.3 Verification and introduction of technology for converting algae into resin or oil

With respect to the oil obtained by the treatment of algae in subcritical water, we examined its performance as a fuel. **Figure 8** shows that the higher the hydrogen concentration and the lower the oxygen concentration relative to the carbon content of the fuel, the higher is the heat of combustion of the fuel. It was found possible to obtain a high-quality fuel oil comparable in combustion heat (about 30 MJ/kg) to ethanol by treating the algae in subcritical water to cause the dehydration and decarboxylation reactions to take place and by polymerizing the obtained oil by means of condensation.

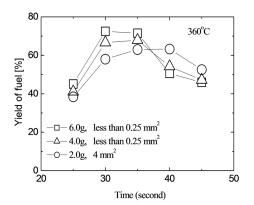


Fig. 6 Relationship between time and yield of fuel

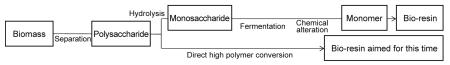


Fig. 7 Production flow of bio-resin

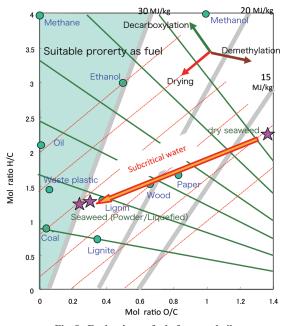


Fig. 8 Evaluation as fuel of seaweed oil Chane of molar ratio (hydrogen, and oxygen/carbon) and combustion heat

3. Conclusion

On the basis of the results of the above series of verification tests, we evaluated the effect of the project to reduce the emissions of CO_2 and discussed the viability and horizontal development of the project as a business.

3.1 Evaluation of effect of the project to reduce CO₂ emissions

Using the measured amount of CO_2 emitted from the materials and heavy machines employed to manufacture the hydrate products and install them in the seas and the calculated amount of CO_2 absorbed by the algae, we estimated the amount of reduction of CO_2 emission made possible by the present project as compared with the construction of a seaweed ground using conventional concrete blocks. The estimated amount of reduction was 13.8 kg- $CO_2/$ m²·year. Based on the standing crop of seaweeds in summer when the seaweeds flourish most, the amount of reduction of CO_2 by the seaweed grounds constructed by the present project was estimated to be 14.6t- CO_2 /year (**Table 2**).

The tasks to further reduce the amount of CO_2 include the improvement of the mixing ratio of raw materials for the hydrates (i.e., reduction of the cement ratio), the establishment of technology for increasing the area of settlement of seaweeds, the maximization of oil yield through establishment of optimum algae treatment conditions, etc. (Table 2).

3.2 Self-dependence and horizontal development of the project

In order for the project that is expected to contribute much to the reduction of CO_2 emissions in the air to become self-dependent in the social system and develop into a new industry, it is considered necessary to tackle the following tasks.

3.2.1 Hydrates

Based on the results of public works performed in the past, the volume of concrete blocks used in port development works, etc. in Hokkaido is estimated to be about 360 000 m³ a year. It can be expected that the hydrates will be able to be substituted for those concrete blocks. In particular, the hydrates that are comparable to concrete in price and performance as a basal object are suitable for ap-

Table 2	Amount	of CO,	reduction
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	Prospect and an achievement ratio		
	Standard physical unit	Amount of reduction	
	$(kg-CO_2/(m^2 \cdot year))$	(t-CO ₂ /year)	
A. Steel-making	4.03 / 3.92	10.9 / 7.8	
slag concrete	(103%)	(139%)	
B. making	3.76 / 5.5	3.71 / 10.9	
seaweed bed	(69%)	(34%)	
C. Oilize	6.0 / 8.0	12.0 / 16.2	
resinification	(74%)	(74%)	
Sum total	13.8 / 17.5	14.6 / 18.7	
Sum total	(79%)	(78%) (A + B)	

plications in which heavy objects like concrete are advantageous. In order to spread the hydrates widely in the market in the future, the major tasks to tackle are the establishment of an organization for supplying the hydrate products, including a production plant that permits using steelmaking slag as the aggregate, and the improvement of quality control techniques, including the temperature control in the manufacturing process.

3.2.2 Seaweed ground restoration project

Japan's seaweed grounds have narrowed down 40% in the past 30 years. Therefore, in addition to the construction of new seaweed grounds by fisheries infrastructure development projects, the restoration of existing seaweed grounds by fertilization, etc. is called for. Two possible methods for restoring seaweed grounds are fertilizing damaged seaweed grounds for effective use of existing basal objects and converting unused beaches into seaweed grounds.

The major tasks to tackle in the future are: establishing a method for calculating the cost performance of projects; building a system not confined within the conventional framework of public projects (creation of employment by agriculture and fisheries + environment + industry); and improving the accuracy of evaluation of CO_2 absorption by the oceans, especially seaweed grounds, which has lower evaluation accuracy compared with the evaluation accuracy of CO_2 absorption by forests.

3.2.3 Converting seaweeds into oil/resin

In the project under review, converting seaweeds into oil is at the stage of basic research on a laboratory scale. From the standpoint of verifying the process for actual oil production in the future, it is necessary to collect such engineering data as the reaction temperature, pressure, flow rate (reaction rate), and slurry consistency; further, it is necessary to optimize the balance between oil properties (performance), cost, etc and discuss the reduction, effective utilization, etc. of water-soluble organic matter and solid products occurring from the process. With respect to the conversion of seaweeds into resin, we intend to carry on our research since it is an important technology from the standpoint of enhancing the value added of chemical application of seaweeds.

Acknowledgments

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Reference

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