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FIELD TEST CONCERNING CHARACTERIZATION OF HUMIC SUBSTANCES DEPOSITED ON THE BOTTOM OF DAM RESERVOIR AND THEIR EFFECTIVE UTIILIZATION

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ABSTRACT

This research was presented Question 89, “Management of Siltation in Existing and New Reservoirs”, in the Technical Session of the 23rd Congress of the International Commission of Large Dams (ICOLD), which was held in Brasilia, Brazil, on 27 May 2009. (21~29 May)

The research confirms/reveals that the environmental problems of concern exist universally since a number of geographically diverse countries, e.g. Argentina and Vietnam, inquired about these issues and showed a keen interest in our research on the management of siltation.

Our research group had conducted actual experiments on an “elution unit” containing dam-accumulated ferrous-humates (Fe-HS). These experiments were carried out at the coast of Miné-cho Tobu, Tsushima, Nagasaki, in November 2008 with sediment taken from Nita Dam in Tsushima, Nagasaki Prefecture.

Our group confirmed, by results of experiments conducted on the ocean bed, that by the effect of FE(II) accumulation within the dam, the growth of seaweed on the ocean bed expanded over a wider area.

In considering the above achievement, this paper elucidates the analyzed results of the Nita Dam sediment and fermentation mechanism, while conducting an outdoor elution test on Nita Dam sediment by actual sea water and elucidates the spreading speed and sustainability of Ferrous-humates (Fe-HS), which had been produced on the reservoir bed.

Thus, it is the experiment in actual sea-water that demonstrated a significant contribution to the earth's environment: by 1) the fixation of CO2 caused by promoting seaweed growth on the ocean bed, as well as by 2) the effective utilization of sediment found in a reservoir bed.

1. ANALYTIC RESULTS OF HUMIC SUBSTANCES IN SEDIMENT AT THE BOTTOM OF NITA DAM, AND ITS FERMENTATION MECHANISM

1.1. INTRODUCTION

Nita Dam, part of the Nita River water system, is located in Tsushima City, Nagasaki Prefecture. It is a concrete gravity dam maintained by Nagasaki Prefecture to provide a reservoir for the collection and regulation of rainwater, and for flood control.

Some 30 years have passed since the dam was completed in 1978. According to the natural flora of Tsushima City, the dam is enclosed by a deep forest of deciduous trees which contribute considerable quantities of humic acids to the mud which accumulates at the bottom of the dam reservoir.

In this sediment are contained humic acid Iron-humates (Fe-HS) which are essential for algae to grow in the sea. Significantly, this is the most effective humic acid iron for recovery.

In fiscal year 2008, The New Energy and Industrial Technology Development Organization, under their "Innovation Practical Promotion Project" initiative, extended us a grant to study and develop a practical "barren ground recovery" method.The report, here, details the proceeding and findings of our work so far in this project, emphasizing our focus on an iron acid elution technology using a humic substance deposited into the bottom of Nita Dam reseservoir. Included are details of the collection and analysis processes, and aspects of the fermentation mechanism of the Nita Dam sediment.

Sampling stations to collect dam sediment for analysis were established at 3 locations relevant to Nita Dam, which is managed by the Nagasaki Prefectural government. The panorama and reservoir of Nita Dam are shown in Photos-1.

Fig-1

Nita Dam sediment collection sites (Stations 1~3)

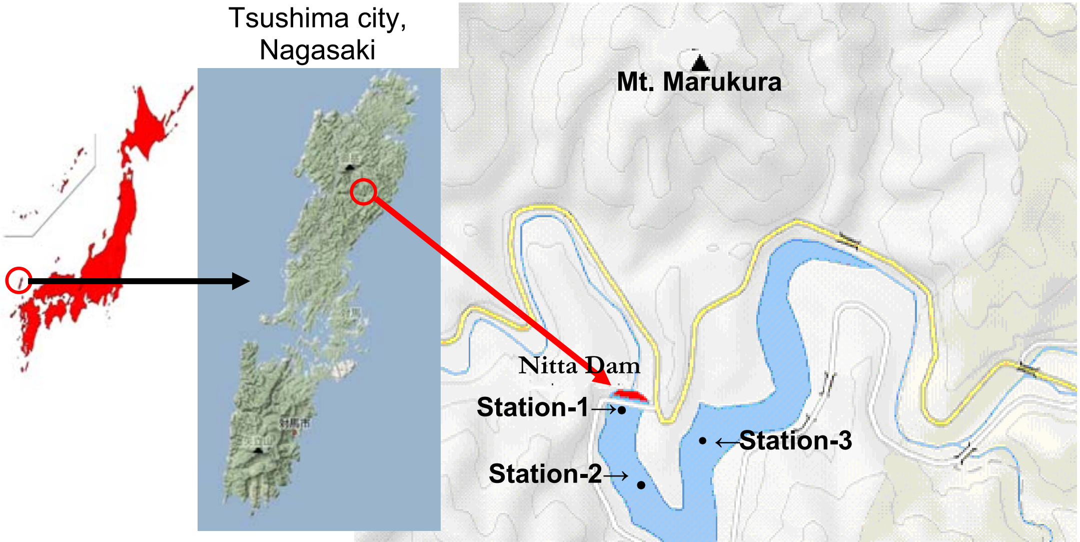

Photo-1 Nita Dam Reservoir

The general characteristics of Nita Dam are shown in Table-1.

Table-1

Some Characteristics of Nita Dam

Location	Kaidokoro,Kami-agata,TsushimaCity,Nagasaki prefecture
River	Nita River Water System; Kaidokoro River
Type of Dam	Concrete Gravity
Dam height / Crest length / Dam volume	33.4 m / 104 m / 33,000 m3
Basin area / Reservoir area	11.1 km2 / 28 ha
Reservoir capacity/Active storage capacity	2,270,000 m3 / 1,990,000 m3
Dam Owner	Nagasaki Prefecture
Construction Contractor	Maeda Construction Co., Ltd.
Date of Completion	1978

1.2. CHEMICAL ANALYSIS OF IRON IN THE SEDIMENT

The sequential extraction method was utilized for analysis of the iron compounds contained in the sediment samples taken from the Nita dam reservoirbed. The procedure and operational analysis are shown in Fig-2. Fraction-C of the analysis is the compound containing the humic substance corresponding to humic acid iron (e.g. Fe-HS). The analysis results for iron are shown in Table-2. The ratio of total iron to Fraction-C was 7.8%~10.9%. This value is larger than the Fraction-C found in 2008 at Dorobe Dam, and the Fraction-C found in 2007 at the Ainumanai Dam, both of which were reported at the last Convention in Brazil.

Fig-2.
Scheme for the Sequential Extraction Analysis of Iron in the Samples.

Soil Sample (1g)
⇩
0.11 M Acetic acid 5mL extraction
Fraction-A (iron-exchangeable)
⇩
pH 2, 0.1 M Hydroxyl-ammonium hydrochloric acid salt
Fraction-B (oxides)
⇩
30% H_2O_2 ⇨ Iron-Fumates
Fraction-C (organic) (Fe-HS)
⇩
HCl/HNO_3 (3/1 = v/v) extraction
Fraction-D (other minerals)

Table-
Iron Content from Analysis Results

Sample from	Fraction-A	Fraction-B	Fraction-C	Fraction-D
Station-1	0.38	3.38	7.77	81.24
Station-2	0.43	3.58	7.98	82.19
Station-3	0.25	2.83	10.85	81.07

1.3. RESULTS AND DISCUSSIONS OF GENERATION MECHANISM FOR THE HUMIC ACID IN SEDIMENT AT THE BOTTOM OF NITA DAM RESERVOIR .

The humic acid sediment samples gathered from the 3 sample stations were extracted and refined by methodology [1] recommended by the International Humic Substance Society.
The structural characteristics of the humic acid in the sediment was clarified and the generation mechanism was studied according to several methods: organic element

analysis, amino-acid analysis, the solid CP-MAS 13C NMR spectrum, molecular weight analysis, and by pyrolysis gas chromatography.

(a) Fixed quantity of humic component

Table 3 shows the content ratio of humic acid (HA) and Fulvate acid (FA) in sediment at each collection station. The humic substance (HS) was about 20~23% of organic carbon in the sediment. The content of HS was 23% at Stations-1 and -2, although Station-3 indicated a content of only about 20% which is somewhat lower in value. In both cases, the HA content was greater than that of FA, and about 80% of the HS contained HA.

Table-3
Humic acid and Fulvates acid contained in the humic substance.

Sample	Total Organic Carbon Content	HS Carbon Content	HA Carbon Content	FA Carbon Content	Non-Humic Carbon Content	FA/HA
	rate (%)	rate (%)	rate (%)	rate (%)	rate (%)	
Station-1	3.59	23.53	19.53	4.00	4.27	0.21
Station-2	3.39	23.24	18.61	4.63	4.99	0.25
Station-3	4.49	19.61	16.33	3.28	3.46	0.20

(b) Element composition and amino-acid composition in the Humic Acid

Table 4 shows the content analysis of organic elements in HA. As a parameter to show the degree of maturity of HA, the N/C mole ratio can be enumerated. But this brings into consideration the fact that Station-3 (0.062) is low as compared to Stations-1 and -2 (0.080, 0.075), and that at Stations-1 and -2 the generation of HA has a higher degree of fermentation.

Table-4
Elemental compositions of HA

Sample	% C	% H	% N	% S	% O	% ash
Station-1	50.13	5.43	4.65	1.08	37.78	0.93
Station-2	51.09	5.46	4.46	1.12	37.43	0.44
Station-3	50.36	5.14	3.67	0.91	39.02	0.90

Table-5 shows the composition analysis results for amino acid. For the gross weight of amino acid, Station-3 registered a low value as compared to Stations-1 and -2 and this corresponded to the trend in N/C evaluated for elemental composition. One might easily presume this wide difference is related to the content values for sulfur and cystine, provided that activity by an anaerobic bacterium like the sulfuric acid reduction bacteria in the reservoir bottom participates in generation of the humic acid. However, there were no big differences between samples concerning the sulfur content ratio in the element composition and the values of cystine. The basic amino acids (lysine, phenyl-alanine, and arginine), which especially had two or more amine parts, did indicate high values at Stations-1 and -2 in comparison to Station-3, although the nitrogen content functional group in the amino acid acted as a ligand for the iron (II). Further, it was thought the carboxyl group was important as a ligand since the figures for the glutamatic acid, which had two carboxyl groups at Stations-1 and -2, indicated high values.

Table-5
Amino acid ratios in the content of HA samples

Rate: mg g-1

Code	Name	Station-1	Station-2	Station-3
Asp	aspartic acid	26.3	25.5	21.6
Thr	threonine	12.9	12.4	10.0
Ser	serine	10.2	9.8	8.0
Glu	glutamic acid	20.8	19.7	16.0
Gly	glycine	14.2	13.9	11.5
Ala	alanine	13.8	13.4	10.9
Cys	cystine	1.1	1.0	0.9
Val	valin	12.5	11.9	9.9
Met	methionine	2.2	2.1	1.6
Ile	iso-leucine	9.1	8.7	6.9
Leu	leucine	13.9	13.2	10.5
Tyr	tyrosine	6.6	6.5	4.9
Phe	phenyl-alanine	9.4	8.9	7.1
Lys	lysine	8.9	9.1	7.1
His	histigene	5.0	4.9	3.9
Arg	arginine	9.3	8.7	6.7
Pro	phosphorus	10.9	10.3	8.6
Total Amino Acid		187.0	180.0	146.0
Code	Name	Station-1	Station-2	Station-3

(c) Analysis of the structural parts by pyrolysis GC/MS

An elucidation of the elemental and amino acid composition, only by content ratio, is difficult. Although the origin of the amino acid, which constitutes the humic acid, is considered to be a metabolic product of microorganism activity or of other living organisms. The humic acid was analyzed, and then the structure was analyzed by pyrolysis GC/MS, and the constituent elements which originated from the biological activity were analyzed. In Fig-3, the group of compounds identified by pyrolysis GC/MS is presented, and the ratio of each group is shown in Fig-4. Here: the phenols (A); the polysaccharides (B – a toroidal ketone is detected as a pyrolysis product); the phenolic acids (D); and the terpenes (G) are all originated from the lignin of terrestrial plants, the cellulose, and wax. The compound which originates from biological activity is a nitrogen-based compound C. The nitrogen-based compound is the smallest in samples from Station-2 but does not show much change in Stations-1 and -3. This result did not follow the rating of amino acids analysis. Therefore, it can be concluded that the origin of the nitrogen content compound is not only an amino acid. Indole derivatives are enumerated as nitrogen-based compounds which are well known as pyrolysis products of amino acid. This corresponded well with the rank of amino acids, analyzed at 4.0% in Station-1, 2.6% in Station-2, and 1.1% in Station-3. Since amino acid is known to be generated by fermentation, by a reduction microorganism under an ammonia coexistence, it would seem that the reduction microorganism contributed to the generation of humic acid at Stations-1 and -2.

The depth of Station-3 is thought to be 4.3m, which is much shallower than Station-2 (9.3 m) and Station-1 (12.5 m). And since the oxygen containing body of water flows shallowly in from the river, it would seem that Station-3 does not exhibit anerobic conditions differing significantly from Stations-1, -2. Although the phenol acids of D are marker substances, originating from the lignin of terrestrial plants, they would be reduced to ketone and aldehyde by the action of living organisms or non-living chemical influences in the reduction environment. In Fig-3, the environment of Stations-1 and -2 is thought to be anaerobic because it is considerably larger than Station-3 and the large decrease of D is seen greatly at Stations-1 and -2.

On the other hand, the saturated and unsaturated fatty acids of E and F are known as biomarkers which show the activity of anaerobic bacteria. In general, the unsaturated fatty acids indicate lipids, which originate from living organisms (e.g. the cell walls of microorganisms), while the saturated fatty acids are rather a metabolic product of the microorganisms. Station-3 measures it at 1.05 and Stations-1 and -2 have increased some to 1.15 when the ratio of each collection station of saturated fatty acid E and unsaturated fatty acid F is calculated. From this result, it becomes clear that microorganisms are more active at Stations-1 and -2 than at Station-3, and the metabolic product of these microorganisms and of the compounded organisms are greatly participating in the generation of humic acid.

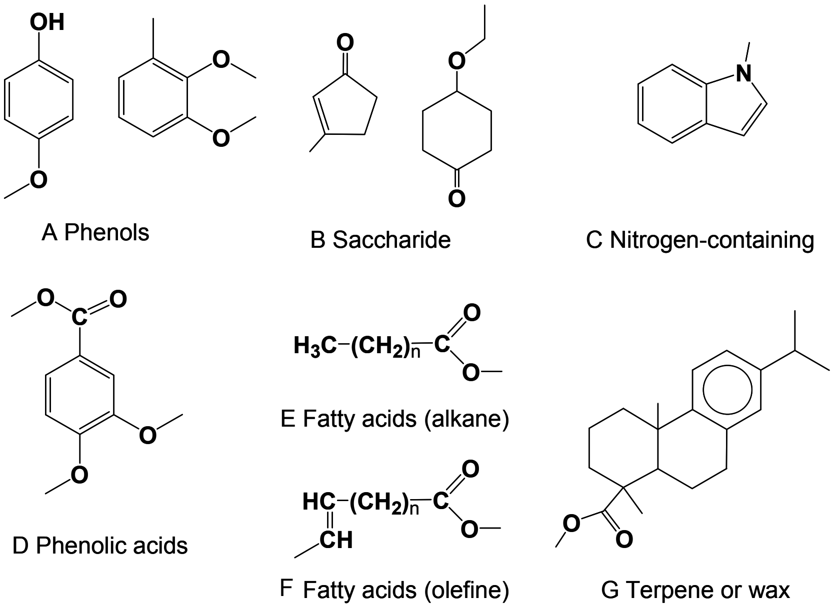

Fig-3

Pyrolysis product of HA detected by pyrolysis GC/MS.

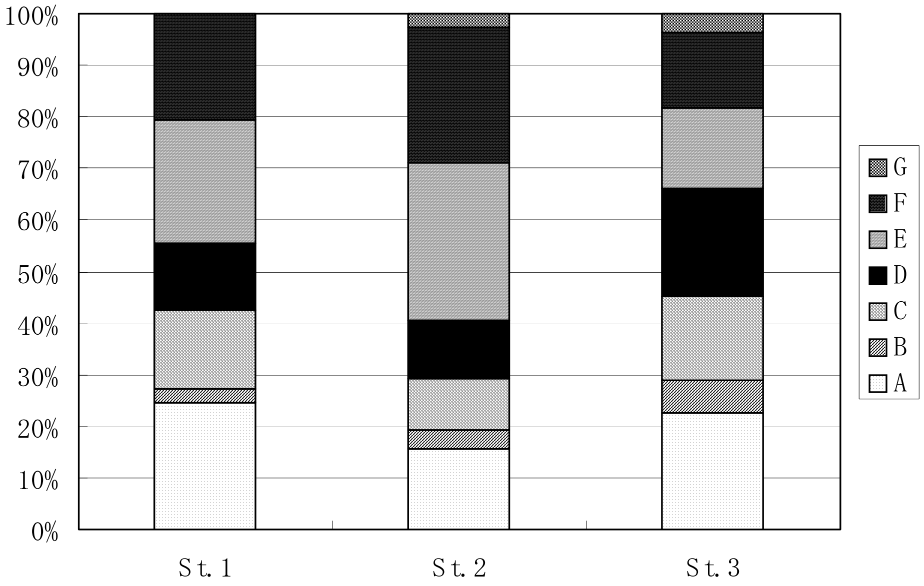

Fig-4

Transition of pyrolysis product in each collection station.

[1] M. Fukushima, K. Yamamoto, K. Ohtsuka, T. Aramaki, T. Komai, S. Ueda, K. Horiya, 2009. Effects of the maturity of wood-waste compost on the structural features of humic acids. Bioresour: Technol. 100, 791-797.

[2] M. Fukushima, M. Yamamoto, T. Komai, K. Yamamoto, 2009. Studies of structural alterations of humic acids from conifer bark residue during composting by pyrolysis-gas chromatography/mass spectrometry using tetramethyl-ammonium hydroxide (TMAH-py-GC/MC). J Anal. Appl. Pyrol. 86, 200-206.

2. SUBSTANTIATION EXPERIMENT IN AN ACTUAL SEA ENVIRONMENT

Judging from results of 1-3, the selection of the collection depot for Nita Dam sediment was decided near Station-2 which microrganisms are more active and anaerobic and has comparatively larger C figures. Dam sediment totaling 17m3 was exacated.

2.1. SEABED SITE AND PROCEDURE FOR SUBSTANTIATION EXPERIMENT

A site for conducting the second phase of this experiment was established in the Matsushima district of Tsushima City (Mine cho-Toubu) (Figs 5~6). 6 cuboid gabions were submerged into the sea water, each containing 15 elution units containing iron fulvates (Fe-HS) that had been excavated from the dam Reservoirbed. Details of the immersion site are shown in Fig-6.

Nitta Dam

Dam sediment collection site

Mine-chou Toubu

Coastal Site for the Substantiation Experiment

Immersion Placement date: 17~25 November 2008

Fig-5

Tsushima Sea area for Substantiation Experiment

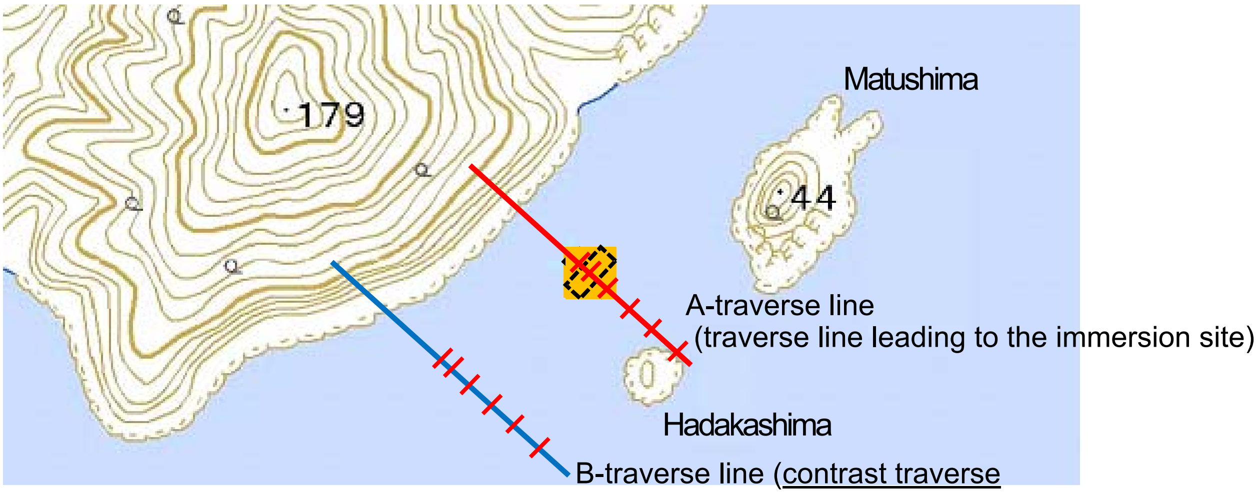

Fig-6
Matsushima Site for cuboid gabion immersion

2.2 PRODUCTION OF ELUTION UNITS FOR THE DAM IRON FULVATES (FE-HS).

The palm tube used for the elution unit has the slowest speed of degeneration among natural fibers (5-7 years in soil, 10 years or more in seawater). It excels in durability, is environmentally friendly, has a comparatively slow speed of water permeability, and is a substance in association with which the elution of Fe(Ⅱ) is gradual. The basic objective had been to create an elution unit (Photo-4) by filling the palm tube with a mixture of iron contained substances (Photo-2) and dam humic substances (Photo-3). Because the elution unit was made of palm husk fiber, whose degeneration speed is the slowest among natural fibers, the elution of Fe(II) was facilitated while maintaining the iron contained substances over a long period of five years or more. The purpose of mixing-in the iron contained substances (steel slag) was to neutralize the acidulous dam humic substance by making steel alkalescency slag, which works as a retarder in delaying the elution speed of high-density humis acid iron.

Photo-2 Iron-contained substance
(steel slag)

Photo-3 Humic substance from the Dam

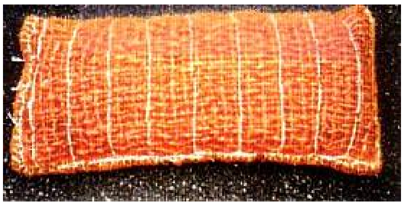

Photo-4 Dam Iron Fulvates (Fe-HS) elution unit

2.3. ACHIEVEMENT

During the first ten days of November 2008, and prior to immersion of the cuboid gabion units, an underwater monitoring investigation (Photo-5) was executed at the intended immersion site just off the Matsushima Coast, of the Minecho Toubu of Tsushima City. This coast was an area where sea algae hardly grew and where, in the middle of November 2008, the bottom of the sea was in a barren condition (Photo-5). By 14 March 2009, after the cuboid gabion units had been immersed for only 4 months, the underwater monitoring imuestigation showed that sargassum macrocarpum was growing thickly around A-traverse line of the cuboid gabion emplacement, and upper branches of the sargassum macrocarpum had already trailed up to the surface of the seawater (Photo-6). Upon further examination, a sargassum fulvellum colony was found, containing such as sargassum honeri, sargassum patens, sargassum ringgoldianum, and sargassum hemiphyllum which, also were observed growing thickly (Photo-7). Moreover, the eisenia bicyclis, too, had increased in number, were growing vigorously, and hatchlings had appeared. Red seaweeds, such as the suinaia japonica setchell and gelidium elegans had grown thickly in the sargassum fulvellum colony where the eisenia bicyclis and other varieties had also generally increased. In the surrounding area, as shown in Photo-8, eisenia bicyclis has vigorously grown up, and on top of the cuboid gabion gloiopeltis furcata and others, such as a lot of eisenia bicyclis and its young sprouts had grown. Other sea algae had begun to grow vigorously on a natural shore reef, and sargassum thumbergii often extended along the rock shelf between the tides. In a deeper site, ecklonia cava kjellman grew in abundance, and new growth was also generated around of 2-3 years age. The growth of infant Ecklonia cava Kjellman on a natural shore reef near the cuboid gabion can be seen in Photo-9.

On 1 May 2009, an additional survey was carried out by the underwater monitoring investigation. By that time, the sargassum fulvellum colony (Photo-10) and the eisenia bicyclis colony (Photo-11) had, since March 14, grown more thickly along A-traverse line, and especially a body of infant eisenia bicyclis were growing on the cuboid gabion (Photo-12). Numerous shoals of fish appeared (Photo-13), and the eggs of cuttlefish (Photo-14) had been laid in the sargassum macrocarpum colony. The profound effect of the dam iron fulvates (Fe-HS) elution unit was confirmed. Observations of these flourishing new colonies will be continued on a yearly basis for several years into the future.

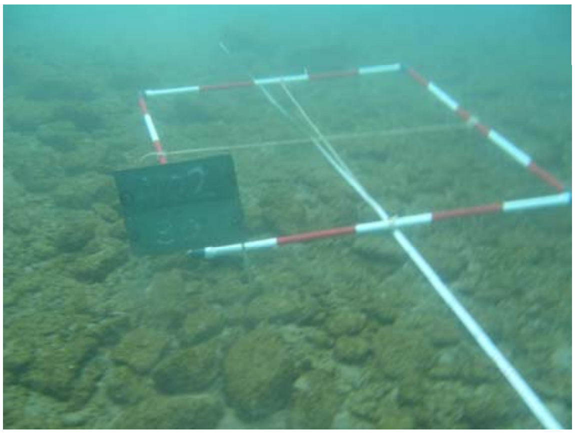

Photo-5 Underwater monitoring investigation

Photo-6 Floating Sargassum macrocarpum algae

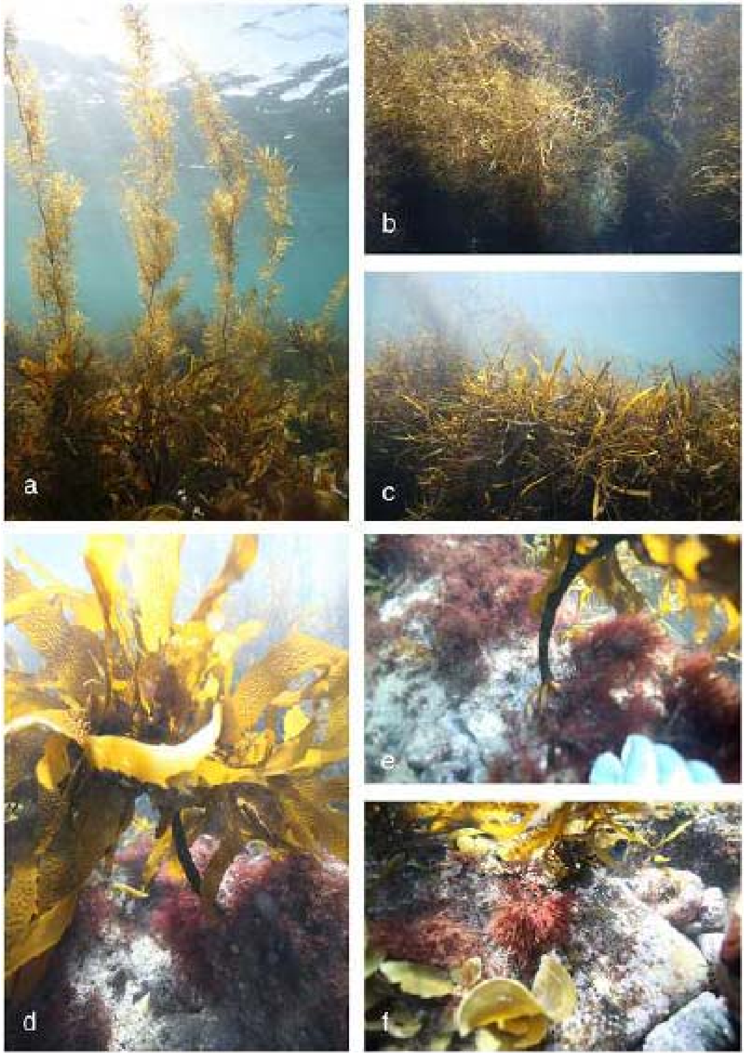

Photo-7 Underwater forest along the A-Traverse line

(a) Sargassum honeri

(b) Sargassum patens

(c) Sargassum ringgoldianum
(d) Eisenia bicyclis
(e) Eisenia bicyclis rhizome (newborn)
(f) Scinaia japonica Setchell seaweed

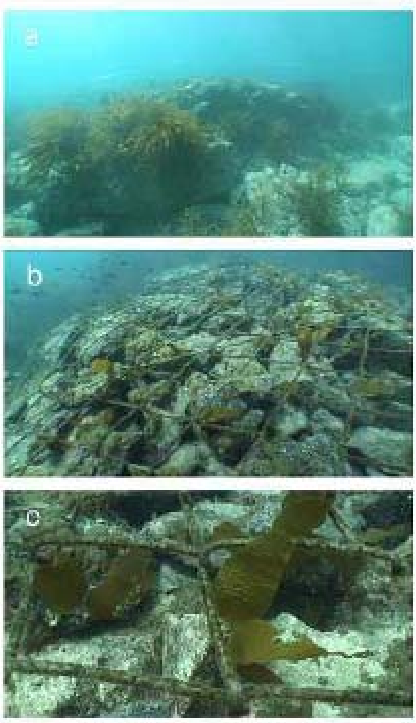

Photo-8 Around the cuboid gabion at the A-Traverse line
(a) Around the cuboid gabion
(b) Newborn Eisenia bicyclis growing on the cuboid gabion
(c) Newborn Eisenia bicyclis growing on the cuboid gabion

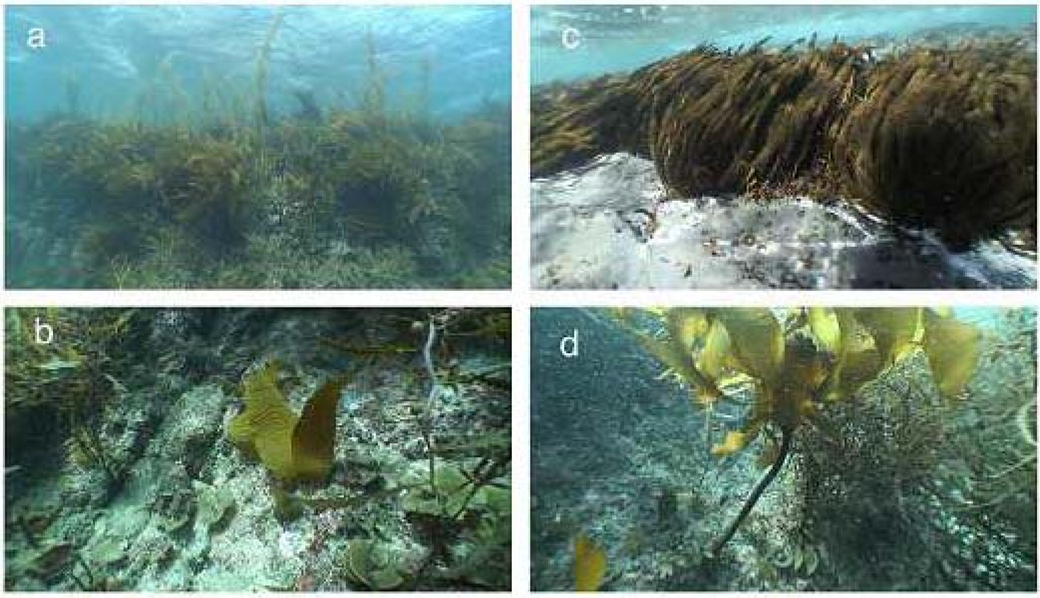

Photo-9 Seaweed on a nearby natural rock reef

(a) Eisenia bicyclis
(b) Eisenia bicyclis newborn
(c) Sargassum thumbergii
(d) Ecklonia cava Kjellman and its newborn (rhizome)

Photo-10 Sargassum fulvellum colony along the A-Traverse line

Photo-11 Eisenia bicyclis colony along the A-Traverse line

Photo-12 Eisenia bicyclis newborn colony

Photo-13 Sargassum fulvellum colony along the A-Traverse line

Photo-14 Cuttlefish egg-blow in a Sargassum macrocarpum colony

3. ELUTION FE(Ⅱ) TEST WITH REAL SEAWATER

3.1 PURPOSE OF THE EXPERIMENT

The effects of this experiment have been confirmed by substantiation examination for the barren ground recovery technology which used steel slag and an artificial humic substance for experimentation in Mashike-cho, Hokkaido. Similar substantiation experiments have being conducted at about 20 or more sites now throughout the country. The base of this Fe(Ⅱ)elution technology is the Fe(Ⅱ) content supply unit. Sustainability evaluation of the effect is presently becoming an important theme.

In order to accurately evaluate the elution characteristics, it is necessary to use actual dam reservoir sediment instead of an artificial humic substance and, again, actual seawater. The substantiation experiment conducted at the Tsushima Aquaculture Examination Laboratory (Tsushima City, Nagasaki Prefecture) began with actual seawater, using actual sediment from Nita Dam.

The aim was to obtain an indicator for optimizing the iron content in the supply unit when using dam sediment. This was done by cross-linking the data and by considering the actual experimental results, the amount of humic substance in the sediment, and the total amount of iron, etc.

3.2. EXPERIMENT METHODOLOGY

Several iron-elution units for the following experiment were set up, one each in the 250L water tanks at the Tsushima City Aquaculture Center (Photo-15), and from these units an iron elution experiment was begun in October 2009.

①Only slag.
②Only sediment.
③Dam sediment + steel slag (volume ratio 1:1)
④Artificial humic substance + steel slag (volume ratio 1:1)

Seawater is continuously supplied to the water tank. About every 15 days, the seawater from the tank is sampled in order to monitor the change in iron density in each water tank. The spectrum brightness method is used for the analysis of iron. Photo-16 shows an elution unit which is set up in such a water tank. Because the size of the elution unit needed here is small, a hemp bag was used instead of the palm fiber bag which, for its qualities of durability, was used in the actual substantiation experiment.

In the elution unit for this experiment, the slag volume (V) of ① was considered as standard; ② was the same (V); and the volumes of ③ and ④ were double (2V).

By comparing the iron elution characteristics of ①,② and ③, the difference in effect when sediment is mixed with slag can be studied. Moreover, the difference of all iron elution characteristics, when the humic substance is included, can be evaluated by comparing ①, ②,③ and ④.

This experiment is presently at a stage where data is being analyzed and studied. When the thesis is finally presented, the results of the experiment will be announced.

Photo-15
Water tank being used for the experiment.

Photo-16
An elution unit set up in one of the water tanks.

4. POSTSCRIPT

This time, as a first attempt in Japan, the analysis and fermentation mechanism of dam sediment (Nita Dam) were elucidated, and the existence of high density iron Fulvates (Fe-HS) where micro bacteria are active in an anaerobic condition in a dam reservoir was confirmed.

Furthermore, the experiment was conducted in a real sea environment (east coast of Tsushima City, west Kyushu region), and only six months later, the sargassum fulvellum colony and the eisenia bicyclis colony had grown in abundance and a large number of fish shoals had appeared, as well as deposits of Cuttlefish eggs, thus substantiating the profound effect of using a dam fulvates acid iron elution unit.

Our study group confirms that iron- humic compound substances from dam sediments are now being used in about 10 sites (Fig-7) around Japan. The ratio of humic acid iron (Fulvates acid iron) at each dam is shown in Fig-8. Our hope is to accelerate the accumulation of actual results for the more effective future use of dam sediments throughout Japan.

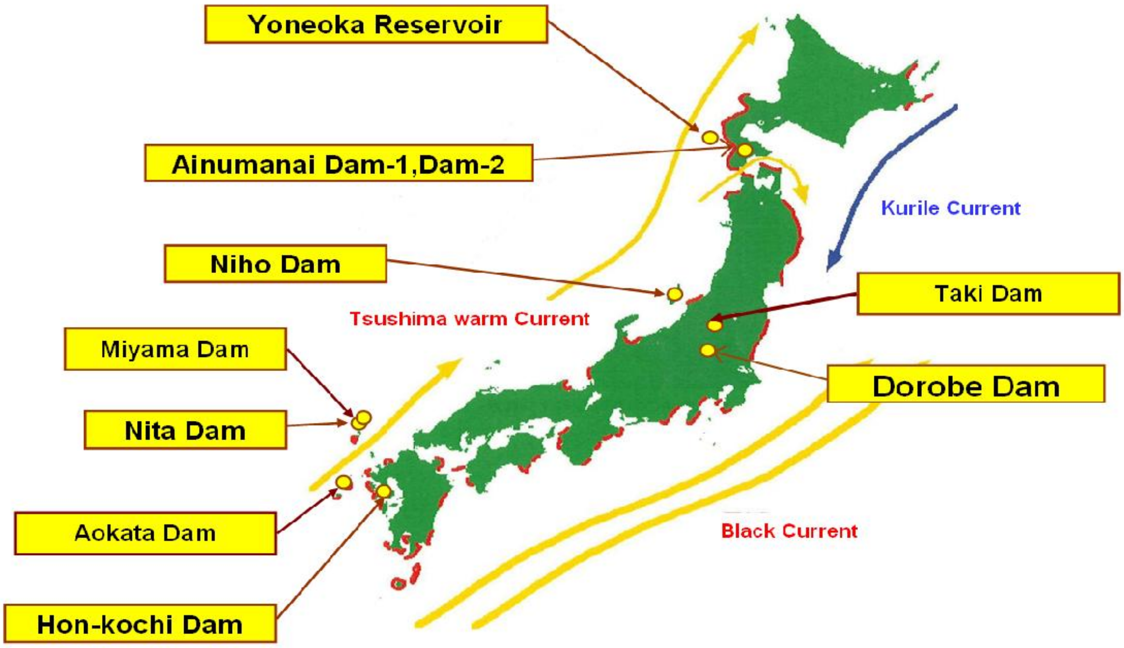

Fig-7
The 10 dams where the harvesting of sediment iron-humus substances are confirmed include:

№	Dam name	Totall Fe	Fraction-C	Totall Fraction-C
		(%)	(%)	(ppm)
		(a)	(b)	(a)×(b)
1	Ainumanai(2006)	4.4	12.7	5.6
2	Ainumanai(2007)	3.6	2.7	1.0
3	Dorobe	2.7	4.1	1.1
4	Hon-kochi	5.2	1.8	0.9
5	Nita	3.2	8.9	2.8
6	Niiho	2.7	3.7	1.0
7	Niiho	3.0	8.6	2.5
8	Yoneoka	2.9	4.6	1.3
9	Ebihara	2.9	2.3	0.7
10	Shizunai	6.1	1.5	0.9
11	Miyama	2.8	6.8	1.9
12	Taki	2.7	8.7	2.3
13	Aokata	4.3	2.6	1.1
14	Uokawa	2.9	4.3	1.2
15		2.0	1.0	0.2

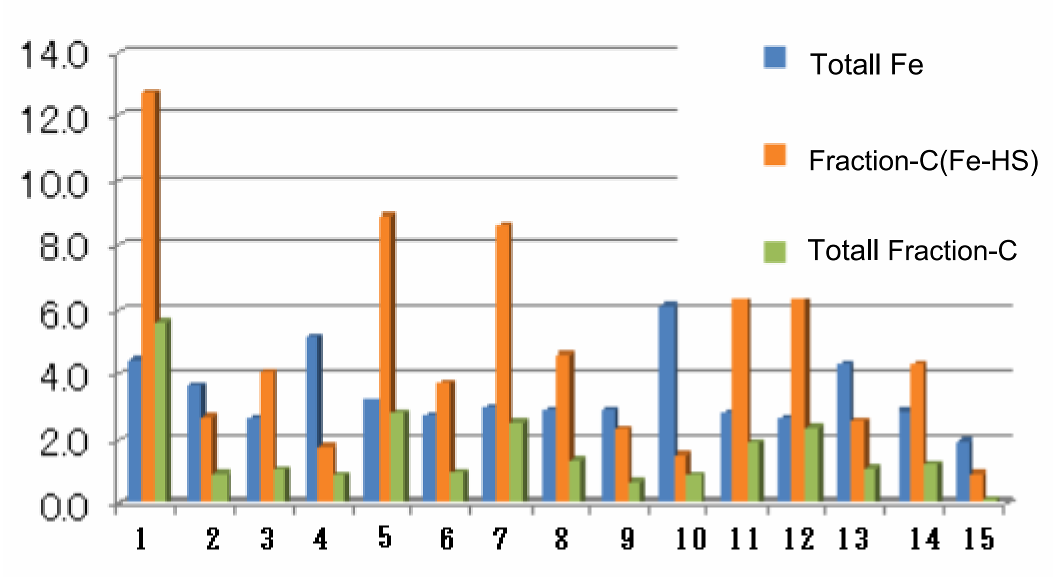

Fig-8

Ratio of Fulvates acid iron in each dam sediment

The system layout in Fig-9 is derived from confirmed results of actual sea environment experimentation. Therefore, this diagram can be considered as a project schematic for practical use. By advancing our understanding through research, new approaches and techniques will emerge and contribute greatly to resolving many global problems of the environment. One such endeavor, through the effective use of dam reservoir sediment, is the fixation of CO2 by promoting the proliferation of algae (sea tangles) along the coast.

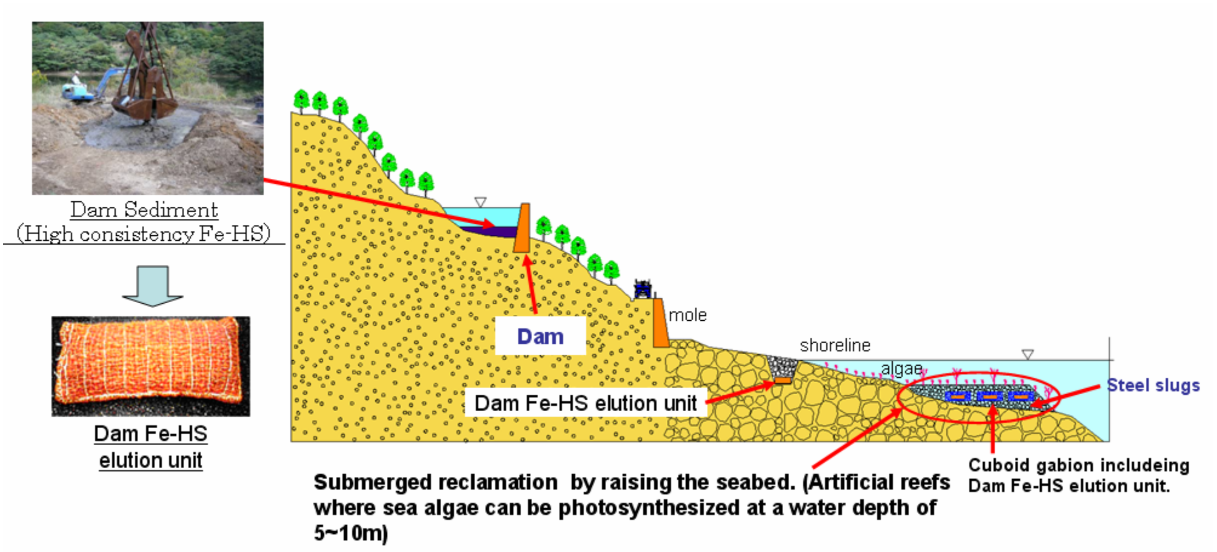

Fig-9

Composite layout showing the practical application of this technology derived from R & D efforts.

Expected Results

Increase of sea resources by sea algae colonies.
CO2 absorption business by sea algae colonies.
Improved water quality by oxygen supply of algae.
Shoreline Preservation by seawood effect of waves.