DOCTORAL THESIS:

Development of Fabrication Technologies for Environmentally Friendly Materials from Dredged Sediments and their Applications for Restoration Enclosed Coastal Seas

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CONTENTS

CHAPTER 1 GENERAL INTRODUCTION

1-1 BACKGROUND

Ago Bay is a typical enclosed coastal sea that is connected to the Pacific Ocean via a very narrow and shallow entrance. The bay, which is world-famous for its cultured pearls, lies in the Mie Prefecture, Japan. Over the past 110 years, the practice of culturing pears in the bay has led to contamination. The expansion of human populations and anthropogenic impacts on sensitive natural systems, such as shallow areas, sea grass beds, and tidal flats, have further increased the input of contaminated materials into Ago Bay, leading to the accumulation of organically enriched sediments on the sea bottom.

In 2000, dredging of the contaminated sea floor sediments was initiated in an attempt to restore the sea environment to a healthier condition and to prevent deterioration resulting from the pearl industry. However, because dredged sea floor sediments tend to emit a horrible smell, finding areas for disposal has become a serious problem. Moreover, the large water content of sediments makes their transport and disposal extremely difficult. The technical feasibility of dredging and disposal, economic and environmental issues, and possibilities for reuse of sediments have not yet been resolved. Thus, the development of an alternative system to treat dredged sea bottom sediments is needed.

The Corps of Engineers manual on beneficial uses of dredged material (USACE, 1987) lists ten broad categories of use: habitat restoration; beach nourishment; aquaculture; recreation; agriculture; land reclamation and landfill cover; shoreline erosion control; industrial use; material transfer for dikes, levees, parking lots, highways; and multiple purposes. Graalum et al. (1999) suggested that dredged material might be to useful for manufacturing topsoil, which would help reduce and recycle waste soil and provide an additional alternative for the long-term management of dredge disposal sites by reducing the amount of land needed for disposal facilities.

Tidal flats are normally located in intertidal zones, important areas that perform many environmental functions such as serving as a habitat for benthic organisms and an area for recreational activities as well as playing a role in water purification and biological productivity. However, in recent years, many tidal flats have been lost as a result of industrial and urban development of coastal areas. According to the Ministry of the Environment, Japan, the total area of natural tidal flats was about 826 km2 in the 1940s; however, by the 1980s, approximately 40% of these natural flats had been lost (Kimura, 1994). Currently, a number of projects are underway to protect and maintain natural tidal flats and wetland ecosystems. Furthermore, efforts are being made to restore damaged tidal flats and create artificial tidal flats to mitigate those that have been lost (Miyoshi et al., 1990; Cofer & Niering, 1992; Ogura & Imamura, 1995; Lee et al., 1998). Mie prefecture, Japan, is involved in one such project as part of the Collaboration of Regional Entities for the Advancement of Technological Excellence (CREATE), organized by the Japan Science and Technology (JST) Agency, under a proposal entitled, "Environmental Restoration Project on the Enclosed Coastal Seas, Ago Bay". Ago Bay in Mie prefecture is one the world's most famous original areas of pearl and oyster culture.

1-2 PURPOSE OF THIS RESEARCH

The main objective in this report is to make clear the ecological impacts through the environmental monitoring of the artificial tidal flat constructed using solidified sea bottom sediments. To date, about 70% of the natural tidal flats in Ago Bay have been lost and destroyed compared with the 1940s (Kokubu et al., 2004). Moreover, the sea conditions in Ago Bay have recently worsened due to the culturing of pearls and oysters, resulting in accumulation of organically-enriched sediments on the sea bottom. Dredging has therefore been performed since 2000 to prevent further worsening of the sea quality in this area. However, since dredged sea bottom sediments tend to give off a horrible smell, the limitation of disposal places has became a serious problem. Moreover, the large water content of sediments makes their transport and disposal extremely difficult. Hence, development of an alternative system to readily treat dredged sea bottom sediments is therefore needed. In the present project, an in situ solidification system for treatment of sea bottom sediments, the "Hi-Biah-System (HBS)", was developed. The solidified sediments were then applied to the construction of an artificial tidal flat in Ago bay. The scheme of beneficial applications for solidified sediments was illustrated in Fig. 1-1. Since its construction, the ecosystem and environmental conditions in the constructed tidal flat have been continuously monitored (CHAPTER 2 and CHAPTER 3). Morover, developing cost-effective, environmentally sound and sustainable management alternatives for the dredged material is a critical issue for the continued operations of the pearl and oyster culture industry' in these bays, which contribute significantly to the Japanese industry. One solution being discussed is to manufacture bricks from the sea sediments. This concept gives priority to waste recovery over its deposit in landfills. The technology of producing bricks from harbour sediments was reviewed as a possible concept for sediments. This report presents the possibility of using sea bottom sediments and the optimization of the raw material components for the fabrication of marine concrete reefs (CHAPTER 4). On the other hand, removal of organic substances that have accumulated due to aquacultural and other industrial purposes in seabed sediments is of great importance in environmental protection. In Ago Bay, more than 10% (by weight) of the sediment is composed of organic substances. Furthermore, humic substances represent large content of these organic substances. In particular, despite the fact that the contamination of seabed sediments with organic substances causes serious problems for the environment, the effects of humic substances on the removal of organic pollutants have not been investigated. The purpose of this report is to investigate the degradation by the ozonation technique of humic substances in seabed sediments collected from two different locations in Japan (Ago Bay and Ariake Bay) (CHAPTER 5). Finally in the last chapter, these field studies focused on the utilization and suitability of dredged sediments to environmental field (CHAPTER 6). Evaluating the performance of a constructed tidal flat, especially the effect of its environmental and ecological impact and beneficial applications of solidified materials were proposed.

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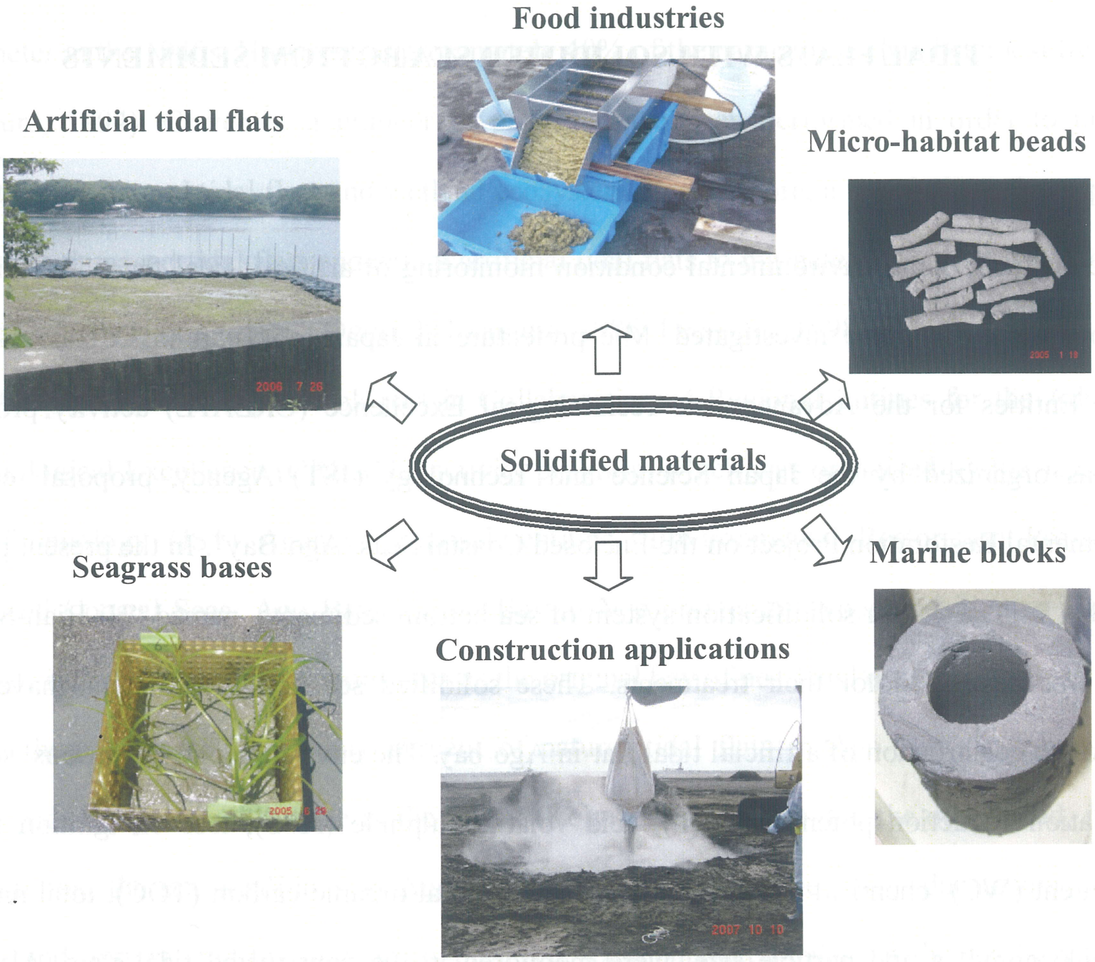

Figure 1-1: Beneficial applications for solidified sea bottom sediments.

CHAPTER 2 CONSTRUCTION OF BIOLOGICALLY PRODUCTIVE ARTIFICIAL TIDAL FLATS WITH SOLIDIFIED SEA BOTTOM SEDIMENTS

2-1 ABSTRACT

The construction and environmental condition monitoring of artificial tidal flat with solidified sea bottom sediments were investigated. Mie prefecture in Japan took part in Collaboration of Regional Entities for the Advancement Technological Excellence (CREATE) activity program, which was organized by the Japan Science and Technology (JST) Agency, proposal, entitled "Environmental Restoration Project on the Enclosed Coastal Seas, Ago Bay". In the present project selected by JST, an in-situ solidification system of sea bottom sediments, named "Hi-Biah-System (HBS)", was developed for their treatments. These solidified sea bottom sediments have been applied to the construction of artificial tidal flat in Ago bay. The environmental conditions, such as pH, oxidation–reduction potential (ORP), acid volatile sulphide (AVS), loss on ignition (LOI), water content (WC), chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (T–N), chlorophyll a and particle size, were monitored in the constructed tidal flats. Also, the number of individuals for the benthos and the growth of short-necked clams in the artificial tidal flats were evaluated. The environmental conditions, the number of benthos individuals, the growth of short-necked clams in the artificial tidal flats were almost similar to those observed in the natural tidal flats.

2-2 INTRODUCTION

The tidal flats normally are located in intertidal zones, which have many environmental functions such as serving as habitats for benthic organisms, water purification and biological productivity, and serving as a locale for recreational activities. In recent years, many tidal flats have been lost as a result of industrial and urban development of coastal area. According to the Ministry of the Environment Government of Japan, the total area of natural tidal flats was about 826 square kilometer in the 1940s. However, approximately 40% of the natural ones had been lost by the 1980s (Kimura, 1994). Currently, a number of projects have been performed in order to protect and maintain the natural tidal flats and wetland ecosystem. Furthermore, a lot of efforts have been made to restore damaged tidal flats and create artificial tidal flats to mitigate the lost ones (Miyoshi et al., 1990; Cofer & Niering, 1992; Ogura & Imamura, 1995; Lee et al., 1998).

Mie prefecture in Japan took part in Collaboration of Regional Entities for the Advancement Technological Excellence (CREATE) activity program, which was organized by the Japan Science and Technology (JST) Agency, proposal, entitled "Environmental Restoration Project on the Enclosed Coastal Seas, Ago Bay". Ago Bay in Mie prefecture, whose position is illustrated in Fig.2-1, is the world's most famous area as the original bay of pearl and oyster culture.

In these days, about seventy percent of natural tidal flats in Ago Bay have been lost and destroyed, compared with those in the 1940s (Kokubu et al, 2004). On the other hand, it has been anxious that the sea conditions in Ago Bay have recently become worse due to the culturing of pearls and oysters, and the organically-enriched sediments accumulate at the sea bottom with the culture activity. Therefore, dredging has been performed since 2000, so as not to worsen the sea quality in Ago Bay. Since the sea bottom sediments dredged gave very horrible smell, the limitation of disposal places became the serious problem. Moreover, the large water content of sediments can make more enormous difficulties for their transport and disposal. Hence, it is necessary to develop alternative system, to readily treat the sea bottom sediments dredged, replaced with the disposal methods. In the present project selected by JST, an in-situ solidification system of sea bottom sediments, named "Hi-Biah-System (HBS)", has been developed for their treatments. These solidified sea bottom sediments have been applied to the construction of artificial tidal flat in Ago bay. Furthermore, the ecosystem and environmental conditions in the constructed tidal flat has been continuously monitored.

2-3 EXPERIMENTAL

2-3-1 Solidification method “Hi-Biah-System” of sediments

The in-situ solidification system of sea bottom sediments, “Hi-Biah-System (HBS)”, was constructed, as illustrated in Fig. 2-2. The HBS consisted of main stock tank of sediments, coagulant chamber, reactors 1 and 2 and dewatering section. The treatment capacity was approximately 1~2 m^3/hour. The water content of dredged sediments was 90% by weight. After the treatment with HBS, the content was lowered to 60 wt%.

2-3-2 Construction of artificial tidal flats

The artificial tidal flats were constructed from February to March 2005 in Ago Bay. The positions of the artificial tidal flats were shown in Fig.2-1. The artificial tidal flats were divided into the 5 sections (from E1 to E5). The area of each tidal flat was length 10 m, width 2 m and depth 0.5 m.

E1 section: 1.5 wt% of soil conditioner, which was made of the ash of paper sludge, was used as the coagulant in the HBS. The chemical components of the soil conditioner were CaO 44.2%, SiO_2 26.9%, Al_2O_3 12.7%, SO_3 12.2 % and so on. After the water content of the sea sediments was lessened to 60 wt%, the solidified sediments were mixed the sand obtained from the Ago Bay. The mixture weight ratio between the solidified materials and sand was 3:7. Finally, artificial tidal flats were constructed with the solidified sediments mixed with the sand.

E2 sections: first, the solidified materials with 60 wt% water content were produced in a similar way as E1 sections. After 20 wt% of same soil conditioner was added into the solidified materials, the pellet was formed with the pelletizer, as illustrated in Fig.2-3. The sharp of the pellet was column with diameter 8 mm and length 20 mm. The E2 section artificial tidal flats were produced from the pellets and the sand (weight ratio 3:7).

E3 sections: the artificial tidal flats of E3 sections were constructed from the sand obtained in Ago Bay.

E4 sections: 5 wt% of coagulant, made of the gypsum, was used for the HBS solidification treatment. After dewatering, the sediment water content was 60 wt%. The solidified materials with water content 60 wt% and the sand (weight ratio 3:7) were mixed, and the artificial tidal flat E4 section was constructed with them.

E5 sections: approximately 2 wt% of poly aluminum chloride (PAC) was added as the inorganic polymer coagulant into the sea bottom sediments. After the dewatering, the water content of the solidified materials was 40 wt%. The solidified sediments treated with PAC were mixed with the solidification agents consisting of waste steel slag (20% by weight), then the obtained solidified materials were mixed with sand (weight ratio 3:7). The materials were used for the construction of the artificial tidal flat E5 section. The procedures for constructing the artificial tidal flats are briefly summarized in Table 2-1.

2-3-3 Monitoring of environmental conditions in constructed tidal flats

The monitoring of the environmental conditions of the artificial tidal flats was conducted every four months. For the comparison, the environmental conditions of natural tidal flats near the artificial one were evaluated. The environmental conditions included pH, oxidation–reduction potential (ORP), acid volatile sulphide (AVS), loss on ignition (LOI), water content (WC), chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (T–N), chlorophyll a and particle size. The chemical parameters of the environmental conditions were evaluated for the soil materials, which was core-sampled from surface to 12 cm depth. The amounts of Chlorophyll a were measured in soil materials from surface to the depth of 1 cm. For the evaluation of benthos, the sediments were sieved with the mesh size of 1 mm, and were added into the 10 vol% formalin. The measurement of benthos was subjected to the general methods.

2-3-4 Growth of short-necked clams

The plastic baskets containing 100 pieces of short-necked clams were set into all of the artificial tidal flats. The growth degree of the short-necked clams, such as the mortality, size and weight, was checked every four months. The chemical compositions of clam tissues were measured by the following ways. First, the clam tissues were dried, powdered and accurately weighted. Then, the tissue samples were treated with 4 ml of nitric acid (14 M) and 1 ml of perchloric acid (9 M). After the decomposition, the solution was evaporated and the wetted residue was dissolved into 1 M nitric acid. Finally, the solution was diluted in a 50 ml volumetric flask. The concentration of heavy metals in aqueous solution was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, VARIAN, multi-type Vista-PRO). The amounts of carbon and nitrogen were measured by the CHN corder instrument.

2-4 RESULTS AND DISCUSSION

In the solidification method HBS, the water content of the sea bottom sediments could be lessened down to 60 wt%. The artificial tidal flats were constructed with the solidified sea sediments, as illustrated in Fig.2-4. The seasonal variations for different chemical parameters for the artificial tidal flats are summarized in Table 2-2. In the natural tidal flat (C-3) on April and July, 2006, acid volatile sulphide, chemical oxygen demand, total organic carbon and total nitrogen were larger relative to those obtained in the artificial tidal flats. However, after six months the values for all of chemical parameters in the artificial tidal flats were almost similar to those observed in natural tidal flat. Table 2-3 shows the results of the particle size analysis of the artificial tidal flats. In all of artificial tidal flats, any coagulation of sands could not be observed. Therefore, during these monitoring periods, the artificial tidal flats had almost same chemical parameter values as natural tidal flat.

Fig.2-5 depicts the time course variations of the number of individuals for the benthos in the artificial tidal flats. The number of individuals after one month was nearly zero in the artificial tidal flats. However, the individual numbers in the constructed tidal flats after three months were larger relative to those in the natural tidal flats. Therefore, the good conditions for the ecosystem of the benthos could be formed in the artificial tidal flats with the solidified sea bottom sediments.

Table 2-4 shows the growth of short-necked clams in the artificial tidal flats. After nine months, the short-necked clams in all of artificial tidal flats grew approximately two times by weight. The concentration of metals such as aluminum, arsenic, barium, cadmium, calcium, chromium, cobalt, copper, iron, manganese, magnesium, molybdenum, nickel, lead, potassium, selenium and sodium were evaluated in clam tissues. On aluminum, arsenic, barium, cadmium, chromium, cobalt, copper, iron, manganese, molybdenum, nickel, lead and selenium metals, the concentrations were less than 1 μg/g-dry weight in the clam tissues. Normally the calcium, iron, magnesium, potassium and sodium concentrations were larger than 1 μg/g-dry weight. Therefore, the chemical components in clam tissues were nearly same as general ones. The total carbon (TC) concentration in clam tissues was in the range of 31% to 39%, and the total nitrogen (TN) concentration was in the region of 7.6% to 9.0%. These total carbon and nitrogen concentrations in clam tissues seem to be judged to be the normal values (Katsuyuki, 1995). Consequently, the ecosystem in the artificial tidal flats with the solidified sea bottom sediments may be considered to be almost similar to those in the natural tidal flats.

In the present work, an in-situ solidification system of sea bottom sediments, named "Hi-Biah-System (HBS)", were developed for their treatments. These solidified sea bottom sediments could be applied to the construction of artificial tidal flat in Ago bay. The ecosystem and environmental conditions in the constructed tidal flats were found to be very similar to those in the natural tidal flats present near the same area.

Table 2-1. Brief summary of the procedures for constructing artificial tidal flats.

Section	**E1**	**E2**
Procedure	(1) Addition of 1.5wt% soil conditioner. (2) Dewatering to 60 wt%. (3) Mixing of muddy sediment of (2) and sand with a ratio of 3:7. (4) Construction of tidal flat with the material of (3).	(1) Addition of 1.5wt% soil conditioner. (2) Dewatering to 60 wt%. (3) Addition of 20wt% soil conditioner. (4) Formation of pellet. (5) Construction of tidal flat with pellet of (4) and sand with weight ration 3:7.
Section	**E3**	**E4**
Procedure	(1) Construction of tidal flat with sand.	(1) Addition of 5wt% gypsum coagulant. (2) Dewatering to 60 wt%. (3) Mixing of muddy sediment of (2) and sand with a ratio of 3:7. (4) Construction of tidal flat with the material of (3).
Section	**E5**	**Natural tidal flat**
Procedure	(1) Addition of 2wt% PAC. (2) Dewatering to 40 wt%. (3) Addition of 20wt% solidification agent (waste steel slag). (4) Construction of tidal flat with the material of (3) and sand with weight ration 3:7.	6 points (C1~C6).

Table 2-2. Monitoring of chemical parameters for the artificial tidal flats.

Station	Time passed[#] (month)	pH	ORP (mV)	AVS (mg/g)	LOI (%)	WC (wt%)	COD (mg/g)	TOC (mg/g)	T-N (mg/kg)	Chlorophyll a (mg/kg)
E1	1	8.0	-265	0.059	5.4	33	8.9	6.8	720	0.75
	3	7.6	-94	0.085	5.7	32	9.8	6.8	700	0.76
	6	7.8	-243	0.085	5.4	29	10	8.1	800	0.69
	9	8.0	-357	0.097	4.5	31	10	8.6	1400	3.50
E2	1	8.1	-55	0.026	5.0	34	5.9	5.9	650	0.63
	3	7.4	-55	0.004	5.2	29	5.9	7.7	600	0.57
	6	7.9	-157	0.007	4.7	30	6.2	6.1	600	1.10
	9	8.4	-176	0.032	4.8	32	6.4	5.1	500	1.70
E3	1	7.3	-89	0.001	3.7	22	2.4	2.4	440	0.25
	3	7.5	36	0.032	4.0	17	1.7	1.9	300	0.18
	6	7.2	-154	0.016	3.1	19	2.1	2.1	300	0.34
	9	7.4	-4	0.010	3.5	23	2.5	2.5	400	4.60
E4	1	7.2	-208	0.016	4.8	29	4.9	5.4	680	0.51
	3	6.8	-140	0.030	5.4	27	5.3	6.6	700	0.35
	6	7.2	-196	0.037	4.9	27	5.5	6.8	600	1.40
	9	7.4	-221	0.105	4.9	28	6.6	4.5	600	2.90
E5	1	9.6	-405	0.051	5.5	28	4.5	8.6	770	0.46
	3	8.4	-322	0.079	6.3	25	4.1	7.2	700	0.24
	6	8.1	-247	0.206	6.1	29	5.8	8.9	900	0.74
	9	9.5	-314	0.177	5.6	27	6.5	8.6	700	1.90
B-3	Apr.	7.3	-124	0.016	5.5	27	6.2	6.5	750	0.48
	Jul.	7.5	-210	0.111	5.4	24	6.5	6.6	1000	0.58
	Oct.	7.3	-179	0.126	4.9	23	5.7	7.5	700	0.50
	Jan.	7.6	-151	0.114	4.9	25	5.6	7.6	700	2.60
C-3	Apr.	7.4	-299	0.532	7.0	43	12	12	1200	0.60
	Jul.	7.3	-239	0.575	8.0	47	18	16	1700	0.25
	Oct.	7.4	-282	0.211	4.5	32	6.7	7.4	600	0.40
	Jan.	7.4	-240	0.026	4.8	33	8.0	9.8	700	1.10

[#] The monitoring was performed on Apr. 2005 (1 month), Jul. (3 month), Oct. (6 month), Jan. 2006 (9 month). B-3; artificial tidal flat constructed previously, C-3; natural tidal flat.

Table 2-3. Particle size analysis for the sand in the artificial tidal flats.

Time passed[#] (month)		E1	E2	E3	E4	E5
1	<75μm[a]	35.6%	28.0%	16.9%	36.1%	25.7%
	median[b]	271 μm	292 μm	861 μm	245 μm	636 μm
3	<75μm	45.1%	22.6%	28.8%	26.3%	19.3%
	median	111 μm	986 μm	286 μm	529 μm	1963 μm
6	<75μm (%)	33.3%	20.0%	15.2%	23.4%	20.3%
	median	210 μm	1504 μm	666 μm	480 μm	631 μm
9	<75μm (%)	43.6%	43.3%	29.1%	45.8%	26.0%
	median	107 μm	115 μm	207 μm	109 μm	346 μm

[#] The monitoring was performed on Apr. 2005 (1 month), Jul. (3 month), Oct. (6 month), Jan. 2006 (9 month).

[a] occupancy of the particle with diameter of less than 75μm.

[b] median particle size.

Table 2-4. Growth of short-necked clams.

Station	Time passed[#] (month)	Mortality (%)	Weight (g)	Length (mm)	Height (mm)
E1	0	0	3.8	24.7	18.4
	3	16	8.1±1.3	33.2±2.4	22.9±1.3
	6	52	8.7±1.8	34.2±2.1	23.8±1.5
	9	72	9.9±1.5	35.2±2.1	25.7±3.2
E2	0	0	3.8	24.6	18.5
	3	8	6.7±1.2	31.5±2.1	21.9±1.6
	6	40	8.2±1.7	33.7±2.7	23.1±1.8
	9	40	8.2±1.7	33.7±2.7	23.1±1.8
E3	0	0	3.8	24.6	18.3
	3	24	7.3±1.5	32.4±2.6	22.3±1.7
	6	44	7.8±1.5	32.6±2.8	22.9±1.6
	9	44	8.6±1.3	34.2±1.8	23.8±1.2
E4	0	0	3.8	24.8	18.3
	3	4	7.2±1.2	31.7±3.0	22.4±1.2
	6	24	8.4±1.2	33.7±2.0	23.4±1.4
	9	32	8.9±1.2	34.2±1.8	23.8±1.1
E5	0	0	3.2	24.5	18.3
	3	16	7.0±1.1	30.9±3.0	22.3±2.7
	6	24	7.6±1.6	32.0±2.3	22.5±1.9
	9	24	8.5±1.5	33.3±2.7	23.3±1.6

[#] The evaluation of growth was performed on Jul. 2005 (3 month), Oct. (6 month), Jan. 2006 (9 month).

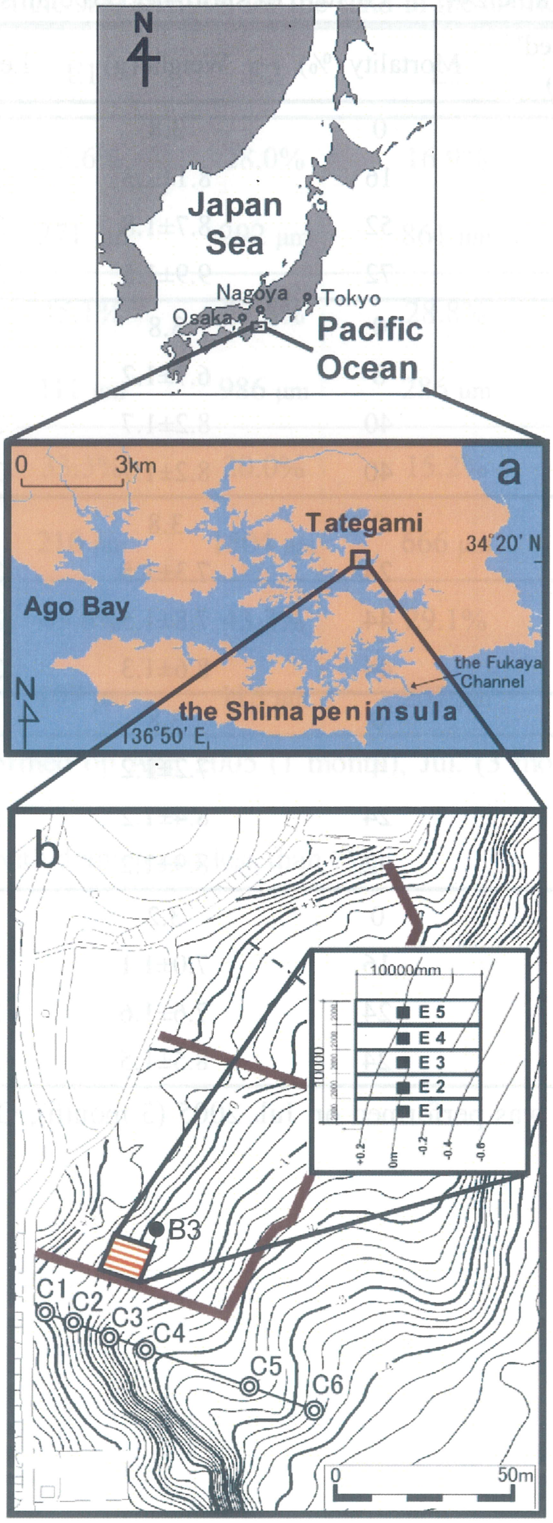

Figure 2-1: Positions of Ago Bay in Mie prefecture and the artificial tidal flats.

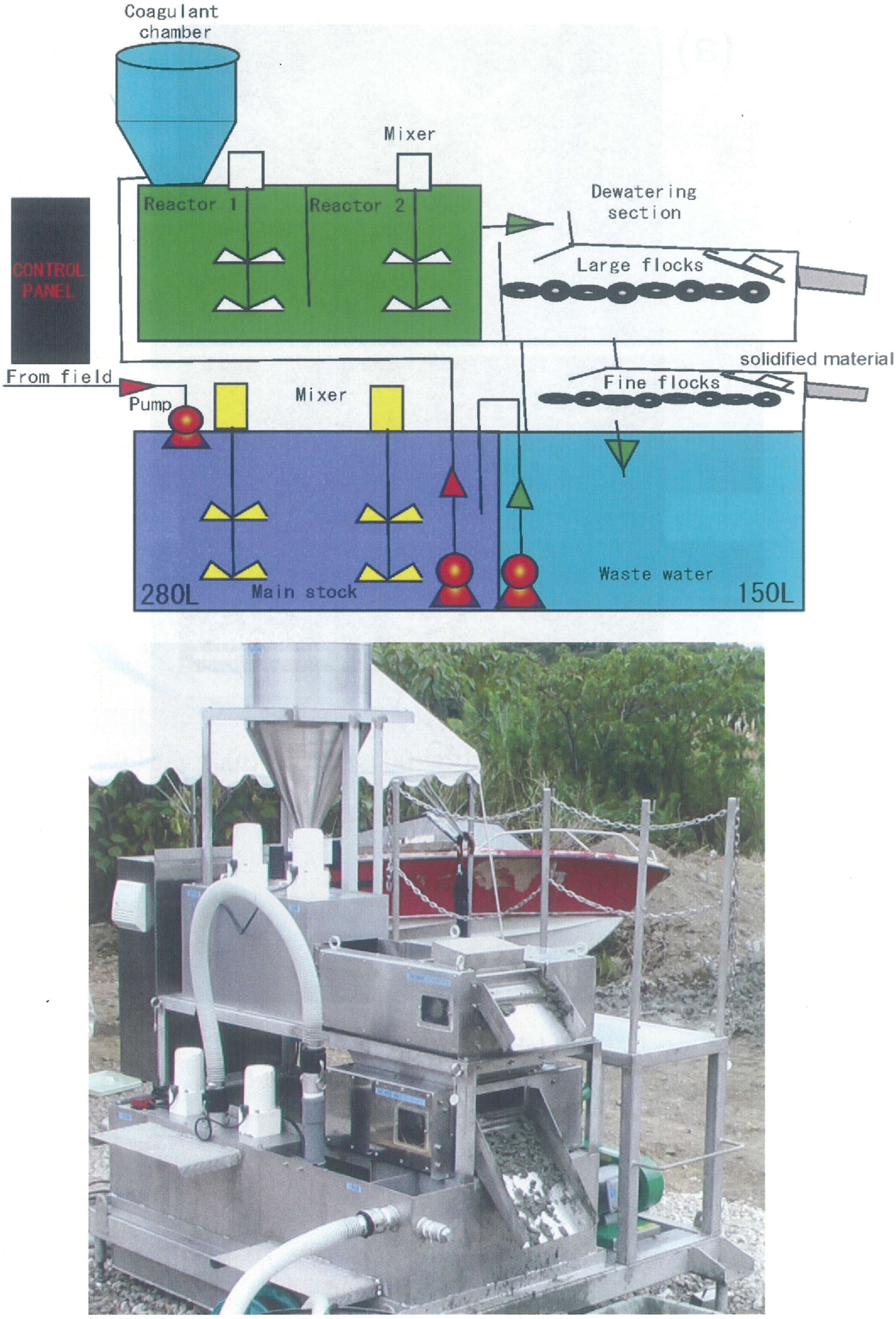

Figure 2-2: Solidification method “Hi-Biah-System” of sediments.

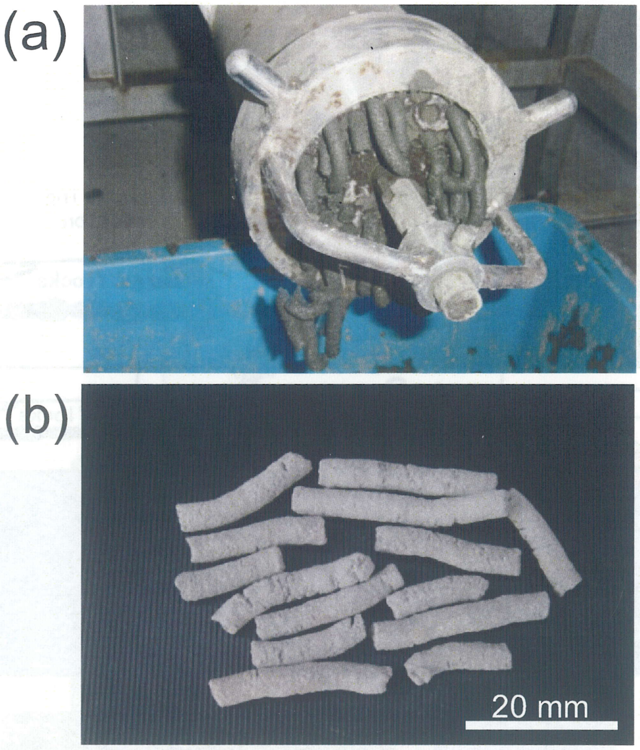

Figure 2-3: Pelletizer (a) and pellet (b).

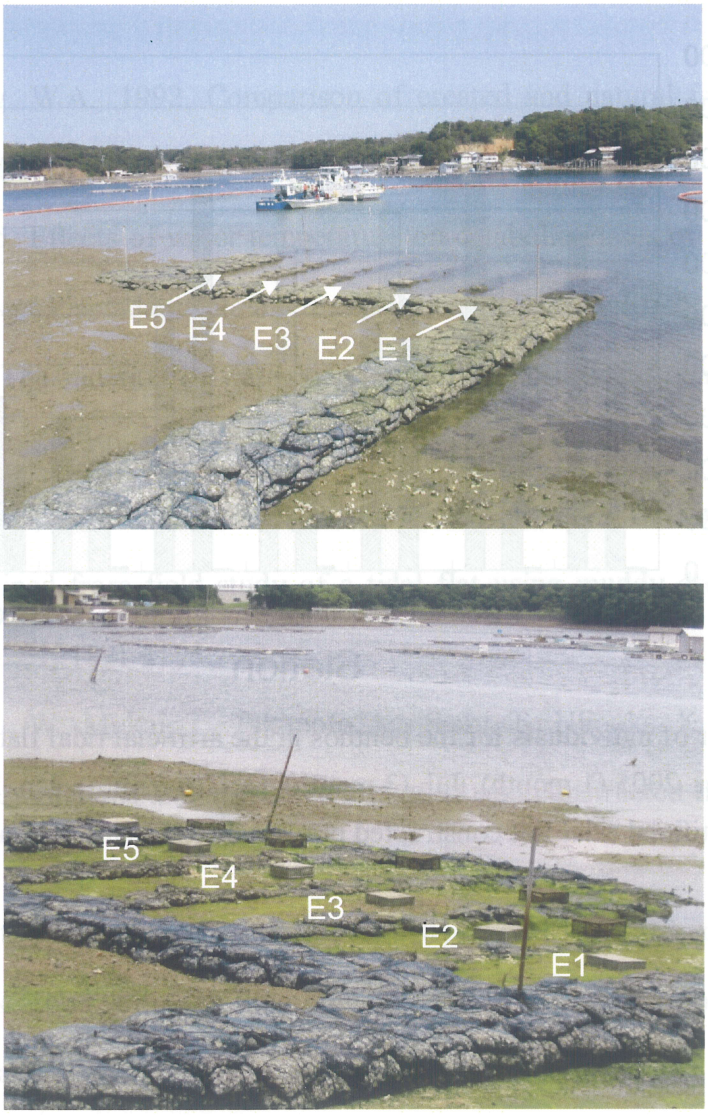

Figure 2-4: Artificial tidal flats.

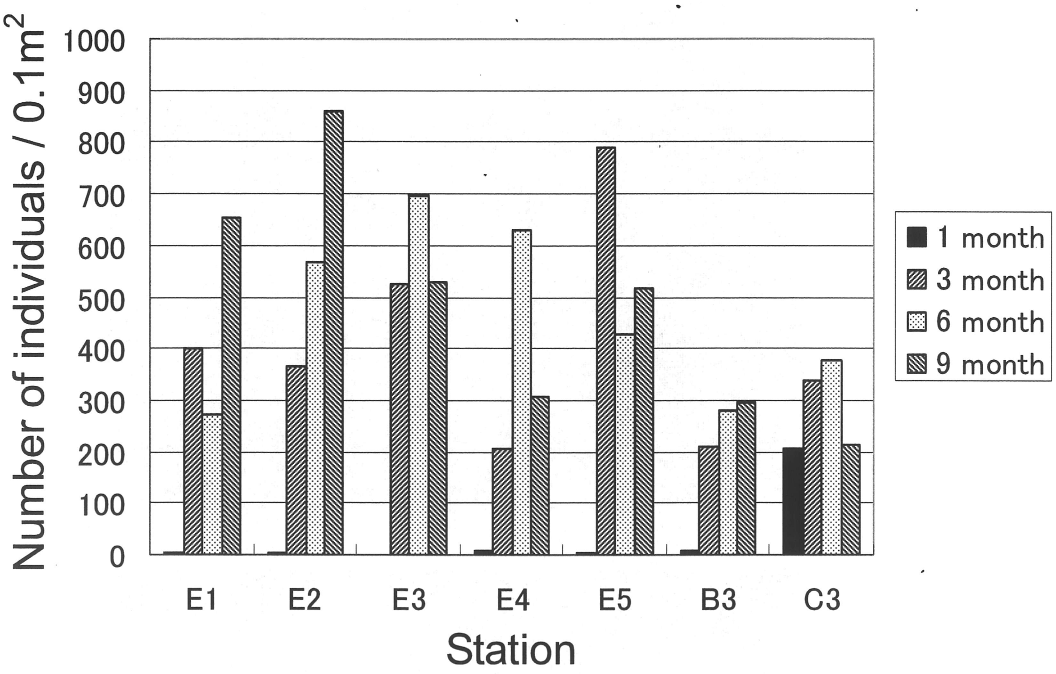

Figure 2-5: Number of individuals for the benthos in the artificial tidal flats. The monitoring was performed on Apr. 2005 (1 month), Jul. (3 month), Oct. (6 month), Jan. 2006 (9 month). B3; artificial tidal flat constructed previously, C3; natural tidal flat.

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CHAPTER 3 ENVIRONMENTAL CONDITION MONITORING OF ARTIFICIAL TIDAL FLAT WITH SOLIDIFIED SEA BOTTOM SEDIMENTS

3-1 ABSTRACT

Ago Bay is a typical enclosed coastal sea that is connected to the Pacific Ocean via a very narrow and shallow entrance. The bay has been organically contaminated by the practice of culturing pearls, which has been ongoing for the past 110 years. To address this problem, a new technology — the Hi-Biah-System (HBS) —, which dewaters muddy dredged sediments and changes the muddy sediments for raw materials of tidal flat, was introduced in 2005. The solidified product from the sediments with the HBS was used to construct the tidal flat. The purpose of this study was to evaluate the environmental conditions of the constructed tidal flat 2 years after its construction. We monitored the physico-chemical (oxidation–reduction potential, acid volatile sulphide, loss on ignition, water content, total organic carbon, total nitrogen, chlorophyll a, and particle size) and biological characteristics of a constructed tidal flat (five sections) and a natural tidal flat (six points). At the same tidal level, the physico-chemical parameters were similar among the constructed and the natural tidal flats. However, the biomass and macrobenthic population were higher in the constructed flat compared to the natural one. According to the findings of this study it can be concluded that the solidified products from the sediments with the HBS could provide useful materials for constructing the tidal coastal environment.

3-2 INTRODUCTION

Ago Bay is a typical enclosed coastal sea that is connected to the Pacific Ocean via a very narrow and shallow entrance. The bay, which is world-famous for its cultured pearls, lies in Mie Prefecture, Japan. Over the past 110 years, the practice of culturing pearls in the bay has led to organic contamination associated with the deterioration of sea water and sediments. The expansion of human populations and anthropogenic impacts on sensitive natural systems (shallow areas, sea grass beds, and tidal flats) has further increased the input of contaminated materials into Ago Bay. Therefore, their situations lead to the accumulation of organically enriched sediments on the sea bottom.

In 2000, dredging of the contaminated sea floor sediments was initiated in an attempt to restore the sea environment to a healthier condition and to prevent deterioration resulting from the pearl industry. However, because dredged sea floor sediments tend to emit awful smell, finding areas for disposal has become a serious problem. Moreover, the large water content of sediments makes their transport and disposal extremely difficult. The economical and environmental friendly dredging and disposal of contaminated sediments as well as possibilities of reusing the sediments have not yet resolved. Thus, the development of an alternative system to treat dredged sea bottom sediments is required for healthier environment.

The Corps of Engineers manual on beneficial uses of dredged material (USACE, 1987) lists ten broad categories of use: habitat restoration; beach nourishment; aquaculture; recreation; agriculture; land reclamation and landfill cover; shoreline erosion control; industrial use; material transfer for dikes, levees, parking lots, highways; and multiple purposes. Graalum et al. (1999) suggested that dredged material might be useful for manufacturing topsoil, which would help to reduce and recycle waste soil. Thus it can provide an additional alternative for the long-term management of dredge disposal sites by reducing the amount of land needed for disposal facilities.

Constructing tidal flats is another alternative use of dredged materials. When the dredged sediment with awful smell is treated by the HBS, the solidified materials from them can not emit the smell. Many tidal flats have been destroyed as a result of industrial, agricultural, and urban development of coastal areas. According to the Ministry of the Environment, Japan, the total area of natural tidal flats was about 826 km^2 in the 1940s. Approximately 40% of these natural flats were destroyed by 1980s (Kikuchi, 1993; Kimura, 1994; Takahashi, 1994). To date, about 70% of the natural tidal flats that existed in Ago Bay in the 1940s have been lost (Kokubu et al., 2004). Tidal flats perform many environmental functions, such as providing a habitat for benthic organisms and playing a role in water purification and biological activity. Currently, a number of projects are under way to protect and maintain natural tidal flats and wetland ecosystems in Ago Bay. Furthermore, efforts are being made to remedy the damaged tidal flats and to create constructed tidal flats for restoring environmental conditions (Miyoshi et al., 1990; Cofer and Niering, 1992; Ogura and Imamura, 1995; Lee et al., 1998).

In the inner area of Ago Bay, large amount of organic matter have accumulated on the sea bed due to eutrophication. It resulted due to the oxygen-deficient water from the bottom to the middle of sea during summer. This phenomenon has occurred in many enclosed coastal seas, such as Tokyo Bay, Osaka Bay, and Ise Bay (Suzuki and Matsukawa, 1987; Joh, 1989; Omori, et al., 1994), as well as in aquaculture areas (Hirata et al., 1994; Tsutsumi, 1995). The hypoxic (or anoxic) water can lead to environmental impacts, such as blue tide (Aoshio) and red tide (Akashio) (Kakino et al., 1987; Takeda et al., 1991). Shallow-water regions such as tidal flats can mitigate these problems; sea grass and sea weed beds act as water purifiers and can play an important role in preventing habitat deterioration and in promoting fish nursery grounds in the inner-bay environment (Takeda et al., 2007).

The Environmental Restoration Project on Enclosed Coastal Seas in Ago Bay — also called the Ago Bay Project — began in 2004 to restore the environmental conditions in the bay under the Collaboration of Regional Entities for the Advancement of Technological Excellence (CREATE) program of the Japan Science and Technology Agency (JST). The goal of the project was to improve the natural self-cleaning capability of the bay by forming constructed tidal flats, shallow-water areas, and sea algae and/or sea grass beds inside the bay.

Hi Biah System (HBS), an up to date technology to treat muddy sea bottom sediments by in situ solidification, was developed in 2005 (Imai et al., 2008a, b; Dabwan et al., 2008). The products by the process, solidified sediments, contain a great deal of mud that was used to construct tidal flats in Ago Bay. Although the condition monitoring in the muddy-enriched, constructed tidal flats play a significant role in the environmental remediation and protection, there is little information on the environmental condition monitoring in the constructed tidal flats. In this study, we continuously monitored the ecosystem and environmental conditions in the five sections of constructed tidal flat and compared it to data from six points of natural tidal flat.

3-3 MATERIALS AND METHODS

3-3-1 Study site

The study site is located in Ise-Shima National Park, a semi-enclosed area around the Shima peninsula that is connected to the Pacific Ocean via a very narrow (1.5 km width) and shallow (25 m water depth) entrance of the bay (Fig. 2-1, CHAPTER 1). The interior part of the bay is complexly divided into many branch bays. The pearl culture industry uses the whole interior area of the bay and the cultivation rafts are spread out like the reticulation; thus, a large-scale dredger can not enter these inner parts of the bay.

The natural tidal flat analyzed in our study lies in the inner part of a branch bay in the Tategami area in Ago bay. The amplitude of the flat varies from 0.5 to 3.0 m and its inclination is 1/10 (Fig. 2-1, CHAPTER 2). The constructed tidal flats were built in the same area.

3-3-2 Solidification method for disposal of sediments

Figure 2-2 (CHAPTER 2) shows the in-situ solidification system. The detailed information has been described previously (Dabwan et al., 2008; Imai at al., 2008a, b). The HBS consists of a main stock tank of sediments, a coagulant chamber, reactors 1 and 2, and a dewatering section. The treatment capacity was approximately 1~2 m^3/hour. The water content of the dredged sediments was 90% by weight. After treatment with HBS, the content was lowered to 60 wt%.

3-3-3 Building the constructed tidal flat

The constructed tidal flat was built from February to March 2005 in Tategami, Ago Bay as shown in Figure 2-1 (CHAPETR 2). It was then divided into 5 sections (E1 to E5), each with an area of 10 m length × 2 m width × 0.5 m depth. Five sections of the tidal flat were constructed by using different materials for exploring the better conditions of artificial tidal flats.

For section E1, the coagulant in the HBS consisted of 1.5 wt% of soil conditioner made of paper sludge ash exhausted from the pulp and paper industry. The chemical components of the soil conditioner were 44.2% CaO, 26.9% SiO_2, 12.7% Al_2O_3, and 12.2% SO_3. After the reduction of water content to 60 wt%, the sediments were mixed with sand obtained from Ago Bay at a ratio of 3:7, and then an area of the constructed tidal flat was built from these materials.

For section E2, solidified materials with 60 wt% water content were produced in a similar way. After adding 20 wt% of the same soil conditioner, a pellet was formed with a pelletizer. The shape of the pellet was a column with a diameter of 8 mm and length of 20 mm. The E2 section of the constructed tidal flat was then built from the pellets mixed with sand (weight ratio 3:7).

The E3 section of the flat was constructed from sand obtained in Ago Bay. For the E4 section, 5 wt% of coagulant consisting of gypsum was used in the HBS solidification treatment. After dewatering, the sediment water content was reduced to 60 wt%, then the solidified materials were mixed with sand (weight ratio 3:7), and an area of the tidal flat constructed.

For section E5, approximately 2 wt% of poly aluminum chloride (PAC) was added as the inorganic polymer coagulant. After dewatering, the water content of the solidified materials was reduced to 40 wt% and the solidified sediments were mixed with solidification agents consisting of waste steel slag (20% by weight) and then with sand (weight ratio 3:7). The resulting materials were used to construct the E5 area of the tidal flat. The sections of the artificial tidal flat illustrated in Figure 2-4 (CHAPTER 2).

3-3-4 Monitoring of environmental conditions in constructed tidal flats

We monitored the physico-chemical parameters and biological characteristics of the natural and constructed tidal flats every 4 months from 28 May 2005 to 20 June 2007. The parameters examined were water content, WC (JIS, 2000a); loss on ignition, LOI (JIS, 2000b); total organic carbon, TOC (Vario MAX CHS, Elementar Analysensysteme GmbH); chemical oxygen demand, COD (JIS, 1998); chlorophyll a (N,N-Dimethylformamide extraction method; Speziale et al., 1984); acid volatile sulphide, AVS (Gas detector tube, GASTEC); and particle size (JIS, 1999). These physico-chemical parameters were evaluated using all of soil materials core-sampled from the surface to 12 cm depth. The amount of chlorophyll a was measured in soil materials from the surface to a depth of 1 cm. Particle size was measured at 3 and 16 months in the natural tidal flat and every 4 months in the artificial tidal flat. To evaluate biomass and a population density of macrobenthos, soil samples were collected within quadrats (25 cm × 25 cm × 25 cm). Subsequently, the samples were sieved through a mesh size of 1 mm and the organisms on the sieve were fixed in 10 vol% formaldehyde (Lee et al., 1998). Organisms then were sorted, identified, counted, and weighed.

3-4 RESULTS AND DISCUSSION

3-4-1 Physico-chemical parameters on the constructed tidal flat

We monitored the physico-chemical environmental conditions on the constructed tidal flat every 4 months for 20 months. Tables 3-1 and 3-2 summarize the results of the particle size analysis of the natural tidal flat and the artificial tidal flat, respectively. In the natural tidal flat, the percentage (abundance ratio) of particles with a diameter < 75 μm had the rough tendency to increase with depth from C1 to C6. At stations C3 to C6 the median particle size was < 75 μm, which illustrates that the natural tidal flat area is a muddy tidal flat. In contrast, only 20–45% of the particles from the artificial tidal flat (except for E3) were < 75 μm. These values were similar to those from stations C1 and C2, but lower than the value from adjacent station C3, which sits at a water depth similar to that of the artificial tidal flat.

No remarkable temporal differences in the muddy fraction percentage in the artificial tidal flat were observed during the 20 months of monitoring. Previous research has documented the movement of fine particles on tidal flats (Yang, 1999; Osborne, 2005; Chang et al., 2007). Although the effusion of muddy fraction (small particle size fraction) was expected in the artificial tidal flat, the observance of no remarkable change in the particles of less than 75 μm between 1 and 20 months may support that this phenomenon did not occurred.

In the estuaries lying at the interface of freshwater and marine systems, organic matter mineralization processes occur (Middelburg et al., 1996). Thus, evaluating these processes over time is important during the construction of man made artificial tidal flats. Figures 3-4 and 3-5 depict the seasonal variations in each of the examined parameters. The WC (a), LOI (b), TOC (c), and COD (d) were almost constant among the monitoring periods. However, the values of these parameters were lower at stations C1 and C2 in the natural tidal flat and at station E3 in the artificial tidal flat, compared to the other stations of both tidal flats. The lower values for WC, LOI, TOC, and COD at stations C1 and C2 may be attributable to the distance from the edge of sea water. The value of chlorophyll a increased over time on the artificial tidal flat. This phenomenon also was observed on the natural tidal flat on the deeper side that sat at the same level as the artificial tidal flat. The tendencies of AVS in the constructed tidal flats were different from the natural one. The reason for them could not be clarified.

3-4-2 Monitoring of macrobenthos on the constructed tidal flat

Evaluating the benthic fauna's response to the constructed tidal flat requires analysis of both numerous changes that occur over space and time (Beukema, 1976; Koh and Shin, 1988; Castel et al., 1989). Figures 3-6 and 3-7 depict the population density and biomass of macrobenthos in the natural (a) and constructed (b) tidal flats over time. On the constructed flat, the population density and biomass were close to zero after 1 month, but after 3 months the population density increased relative to that observed in the natural tidal flat (especially at the same depth level station (C3), as shown by the arrows). On the other hand, the biomass of macrobenthos reached a level similar to that of the natural tidal flat after 6 months. After 20 months of monitoring, despite the temporal increase and decrease, the population density and biomass of macrobenthos in the constructed tidal flat increased relative to that of the natural tidal one. The predominant macrobenthic species in the constructed tidal flat were polychaetes and molluscans. At the deeper stations of the natural tidal flat, the predominant species were bivalves, but the species observed were similar at both tidal flats and the species composition of the two types of flat were not significantly different. These results were similar to data reported previously (Havens et al., 1995; French et al., 2004). These observations for better population and biomass of macrobenthos may be due to useful organic and mineral substances supplied by the solidified sea bottom sediments, which would generate good ecological conditions for benthic animals. However, Herman et al. (2001) reported that the abundance of microalgae is much lower at muddy than at sandy sites, and they hypothesized that high mud content decreases the availability of benthic microalgae. Likewise, Billerbeck et al. (2007) pointed out that benthic photosynthesis was greater in the submerged inner bay with sandy substrate than in the muddy area.

Long-term monitoring is needed to better understand the effects of using these muddy solidified sea bottom sediments to construct tidal flats. To our knowledge, few long-term investigations have been undertaken in the artificial tidal flats (Cammen et al., 1974; Seneca et al., 1976), but available data suggest that the habitat functions (e.g., primary production, organic carbon content) on a constructed tidal marsh would be similar to those of a natural tidal one after several years.

Lee et al. (1988) investigated the physico-chemical and biological characteristics of several natural tidal flats and constructed tidal flats with various types of sandy and muddy conditions in the semi-closed sea environment. They found no remarkable differences in the population density and biomass of macrobenthos between the artificial and natural tidal flats. In contrast, bacterial populations of the sandy constructed tidal flats were significantly lower than those in the natural flats. However, the population density of samples collected from the constructed tidal flat with high silt content was similar to that of the natural tidal flat. Ueda et al. (2000) reported that the sediments containing the silt particles were kept oxygenated and accessible to benthic animals throughout the year on tidal flats and the dominant benthic fauna were larger than those found in adjacent inner bay bed. These literature reports and the experimental data in the present work may indicate that silt particles play an important role in providing habitats for benthic bacteria and biologically active environments for tidal flats.

In the natural tidal flats (Fig. 3-6a and Fig. 3-7a), the water depth increased from C1 to C6 and station C3 was at almost the same depth as the constructed flat (E1 to E5). The macrobenthic population density at stations C1 and C2 was lower than at stations C3 to C6 (Fig. 3-6). C1 and C2 also had lower water content and organic matter content (LOI, TOC, and COD; Fig. 3-4) than other natural stations. These values were lower than those obtained in the constructed tidal flat (except for E3), although the high silt contents was observed in natural tidal flat rather than the artificial tidal flats. The character of the constructed tidal flat at station E3 may be attributed that it was made of only the sand. The organic matter content can affect both population density and biomass of macrobenthos. Although little relation of macrobenthic biomass with the organic matter content could be observed in the present study, it was roughly postulated that the organic matter content in the range of 3% to 7% was moderately effective for increasing the macrobenthic population density, based on the comparison between the artificial and natural tidal flats. Consequently, the present results suggest that it is significant to construct artificial tidal flats by considering not only organic matter content but also water depth.

3-5 CONCLUSION

We developed an in situ solidification system for treatment of sea bottom sediments (the Hi-Biah-System (HBS)). These solidified sea bottom sediments were then used to construct an artificial tidal flat in Ago Bay. The ecosystem and environmental conditions of the constructed tidal flat, which were monitored and compared to a natural tidal flat over the course of 2 years, were found to be very similar to those of the adjacent natural tidal flat.

Table 3-1. Particle size analysis of the natural tidal flat.

Time passed[#] (months)		C1	C2	C3	C4	C5	C6
3	< 75 μm[a]	42.1%	48.2%	64.1%	72.9%	83.1%	56.2%
	median[b]	96 μm	83 μm	41 μm	23 μm	4 μm	43 μm
16	< 75 μm	35.7%	47.7%	67.3%	81.4%	69.0%	75.7%
	median	120 μm	80 μm	31 μm	6 μm	10 μm	6 μm

[#] In 2005, monitoring was performed in Apr. (1 month), Jul. (3 months), and Oct. (6 months); in 2006 in Jan. (9 months), Jun. (13 months), Sep. (16 months), and Nov. (18 months); and in Jan. 2007 (20 months).

[a] Percentage of particles with a diameter < 75 μm

[b] Median particle size

Table 3-2. Particle size analysis of the materials used to construct each section of the artificial tidal flat.

Time passed[#] (months)		E1	E2	E3	E4	E5
1	< 75 μm[a]	35.6%	28.0%	16.9%	36.1%	25.7%
	median[b]	271 μm	292 μm	861 μm	245 μm	636 μm
3	< 75 μm	45.1%	22.6%	28.8%	26.3%	19.3%
	median	111 μm	986 μm	286 μm	529 μm	1963 μm
6	< 75 μm	33.3%	20.0%	15.2%	23.4%	20.3%
	median	210 μm	1504 μm	666 μm	480 μm	631 μm
9	< 75 μm	43.6%	43.3%	29.1%	45.8%	26.0%
	median	107 μm	115 μm	207 μm	109 μm	346 μm
13	< 75 μm	28.0%	36.0%	21.1%	32.5%	26.0%
	median	310 μm	220 μm	340 μm	240 μm	360 μm
16	< 75 μm	33.9%	25.7%	18.3%	31.7%	25.9%
	median	230 μm	330 μm	370 μm	250 μm	340 μm
18	< 75 μm	36.6%	27.5%	20.1%	29.2%	26.0%
	median	210 μm	280 μm	350 μm	240 μm	320 μm
20	< 75 μm	31.2%	31.3%	19.0%	26.0%	22.9%
	Median	240 μm	230 μm	320 μm	260 μm	390 μm

[#] In 2005, monitoring was performed in Apr. (1 month), Jul. (3 months), and Oct. (6 months); in 2006 in Jan. (9 months), Jun. (13 months), Sep. (16 months), and Nov. (18 months); and in Jan. 2007 (20 months).

[a] Percentage of particles with a diameter < 75 μm

[b].Median particle size

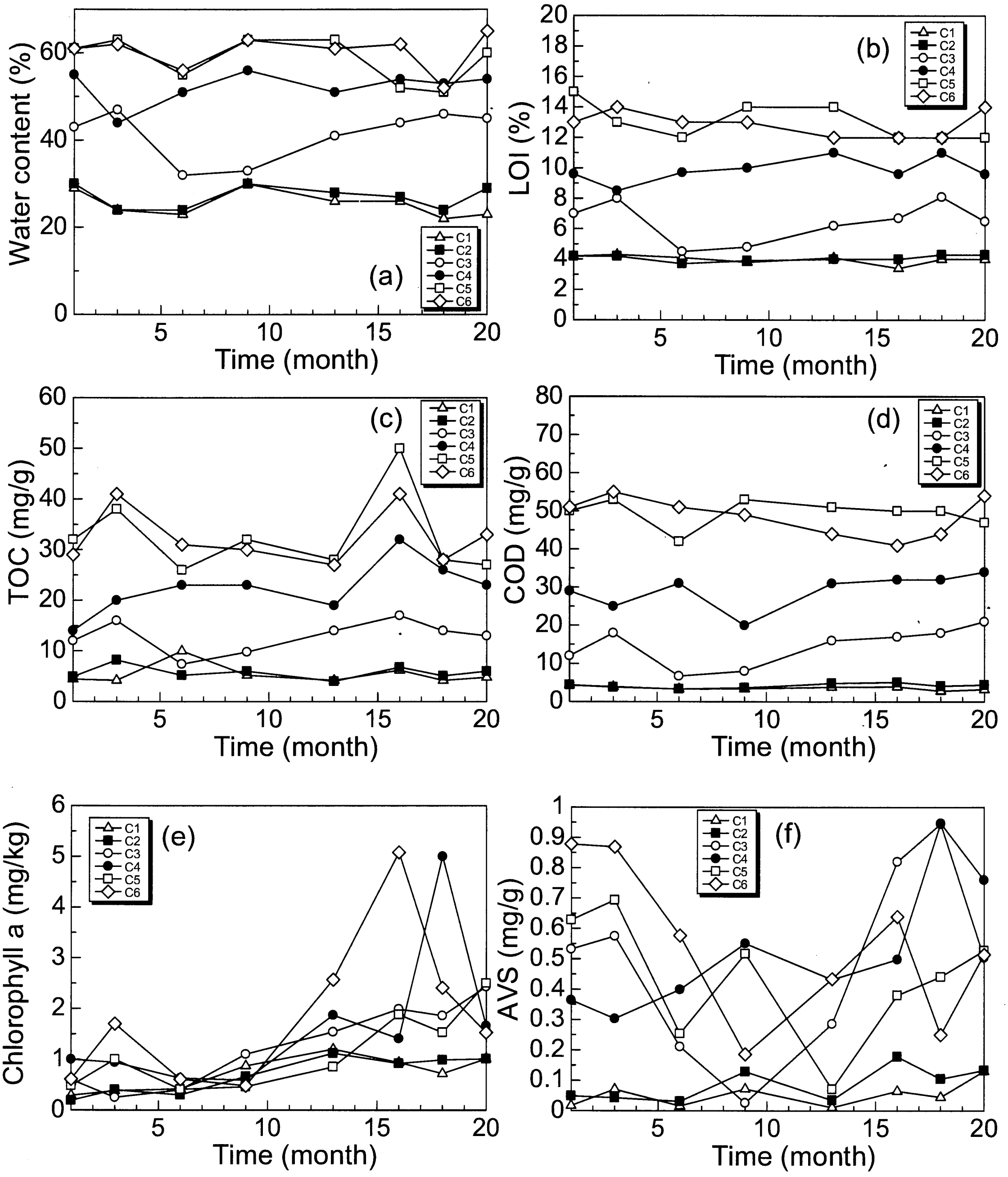

Figure 3-4. Chemical parameters of the natural tidal flat. See Table 3-1 for monitoring dates. (a) WC: water content, (b) LOI: loss on ignition, (c) TOC: total organic carbon, (d) COD: chemical oxygen demand, (e) Chlorophyll a, (f) AVS: acid volatile sulphide.

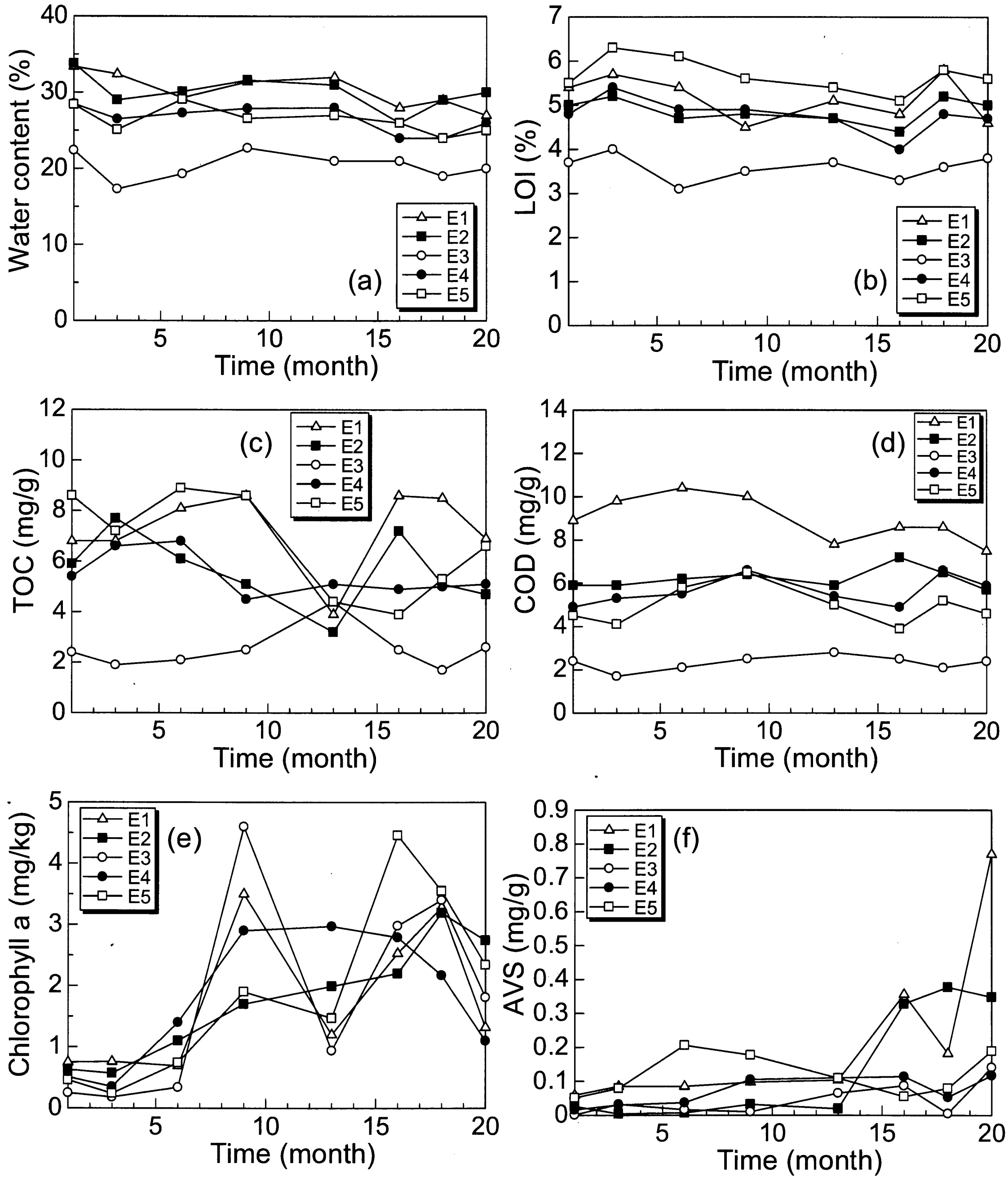

Figure 3-5. Chemical parameters of the artificial tidal flat. See Table 3-1 for monitoring dates. (a) WC: water content, (b) LOI: loss on ignition, (c) TOC: total organic carbon, (d) COD: chemical oxygen demand, (e) Chlorophyll a, (f) AVS: acid volatile sulphide.

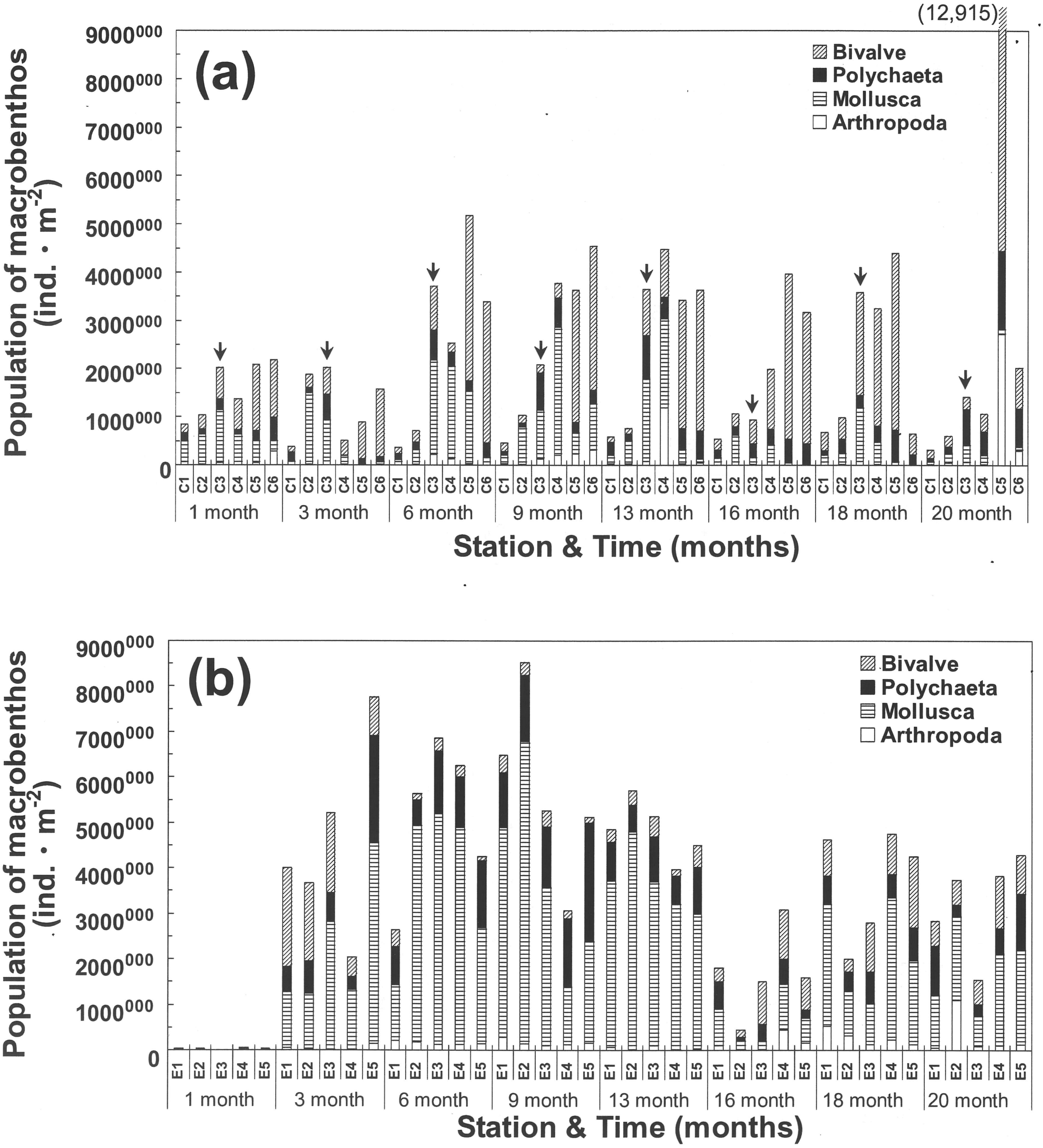

Figure 3-6. Population of macrobenthos in the natural tidal flat (a) and the artificial tidal flat (b). See Table 3-1 for monitoring dates. C1 to C6: the natural tidal flat.

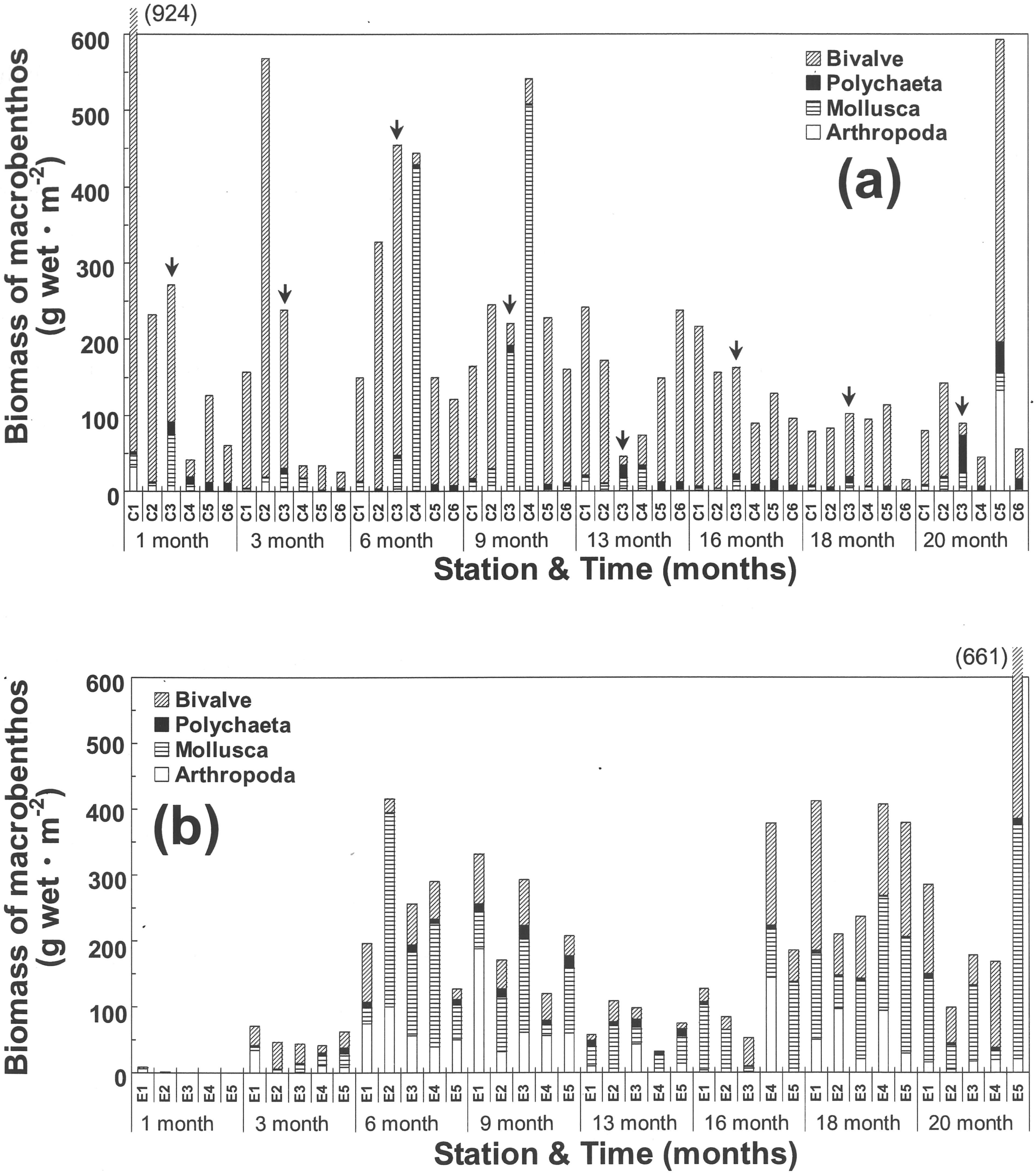

Figure 3-7. Biomass of macrobenthos in the natural tidal flat (a) and the artificial tidal flat (b). See Table 3-1 for monitoring dates: C1 to C6: the natural tidal flat.

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CHAPTER 4 DISPOSAL OF SEA BOTTOM SEDIMENTS BY USE AS RAW MATERIAL FOR CONCRETE ELEMENTS

4-1 ABSTRACT

The possibility of using sea bottom sediments as a substitute for fine sand aggregate was investigated for the fabrication of concrete solids and marine reefs. The proportions of raw materials in the concrete mixture were optimized, and the materials were evaluated with by testing their slump, air content, mass change, total shrinkage and compressive strength. In the short term, i.e. a curing age of 3 to 28 days, the compressive strengths of the concrete materials made with the sediments were better than those of the normal concrete blocks. Furthermore, after 187 days of curing, the compressive strengths were 44, 31 and 12 MPa respectively for the concrete products with a water-cement ratio (w/c) by weight of 0.47, 0.69 and 1.15 using the sediments. When the concrete materials were field-tested in the sea for approximately one year, the blocks were not damaged by the sea environment because the compressive strengths were 48, 33 and 14 MPa with w/c = 0.47, 0.69 and 1.15, respectively. Since the concrete blocks constructed with the optimal mix of raw materials had enough solid strength to be used in the sea, it may be unnecessary to add steel reinforcement to this concrete for the specific purpose of constructing marine reefs.

4-2 INTRODUCTION

The corrosion resistance of concrete is one of the most important factors in the durability of this material. Chloride ions constitute one of the deleterious agents that may cause or promote corrosion of steel reinforcement in concrete. Chloride-induced corrosion of steel reinforcement in concrete structures has been a focus of interest for decades in the field of civil engineering. As a result, a number of investigators have dealt with the influence of chloride ions on the qualities of cement (Shi et al., 2000a; Shi et al., 2000b; Koleva et al., 2006).

Ago Bays in Mie prefecture, Japan is world-famous area as the origin of pearl and oyster culture. However, there is a concern that the sea conditions have recently become worse due to the culturing of pearls and oysters, which has resulted in the accumulation of organically-enriched sediments on the sea bottom. Therefore, dredging of sea sediments has been performed since 2000, so as not to worsen the sea quality in Ago Bays. Since the dredged sea sediments have a horrible smell, the limited availability of suitable disposal places has become a serious problem. Hence, developing cost-effective, environmentally sound and sustainable management alternatives for the dredged material is a critical issue for the continued operations of the pearl and oyster culture industry' in these bays, which contribute significantly to the Japanese industry (Kaneco et al., 2004, 2005; Katsumata et al., 2004; Imai et al., 2007; Dabwan et al., 2007).

One solution being discussed is to manufacture bricks from the sea sediments. This concept gives priority to waste recovery over its deposit in landfills. The technology of producing bricks from harbour sediments was reviewed as a possible concept for sediments in Bremen (Hamer et al., 1999). On the other hand, there is little information on the fabrication of concrete solids using sea sediments as raw materials, due to the corrosion of the steel reinforcement. Recently, Alabadan et al. (2006) have investigated the potentials of groundnut shell ash (GSA) as a partial replacement for ordinary Portland cement in concrete. In the study, although the strength of the control was higher, the replacement of cement with ash up to 30% would be more suitable than others.

If the solid strength of cement is improved by optimizing the raw material components, it may be unnecessary to add the steel reinforcement to the concrete for certain purposes. The present work presents the possibility of using sea bottom sediments and the optimization of the raw material components for the fabrication of marine concrete reefs. This application deals with the utilization of sea bottom sediments as a substitute for fine sand aggregate.

4-3 MATERIALS AND METHODS

4-3-1 Dredged Sea Sediments

The sea bottom sediments in Ago Bay were dredged and collected in March, 2005. The typical chemical components in the sediment were as follows: SiO_2 (51.0%), Al_2O_3 (17.2%), CaO (11.9%), SO_3 (9.6%), Fe_2O_3 (4.5%), K_2O (3.1%), MgO (1.8%) and TiO_2 (0.6%). The main chemical components of the sediments dredged in the present work were very similar to those reported previously in Ago Bay (Kaneco et al., 2004), and the concentrations of toxic metal elements, including lead, cadmium and arsenic, were not a serious problem. Moreover, toxic organic pollutants such as agrochemicals, pesticides and dioxin were not detected in the sediments. The chloride content was 1.63 wt% in the dried sediments. The water content of the dredged sediments was 90% by weight. The "Hi-Biah-System (HBS)" for the in-situ solidification of sediments, was used for the treatment of the sediments (Imai et al., 2007; Dabwan et al., 2007). The HBS consisted of a main stock tank for the sediments, a coagulant chamber, reactors and a dewatering section. The treatment capacity was approximately 1~2 m^3/hour. The soil conditioner (1.5 wt%), made of the ash from burning paper sludge, was used as the coagulant in the HBS. The chemical components of the soil conditioner were CaO 44.2%, SiO_2 26.9%, Al_2O_3 12.7% and SO_3 12.2 %. After treatment with the HBS, the water content was reduced to 60% by weight.

4-3-2 Fabrication of Concrete

The raw materials used in the fabrication of concrete were as follows: Portland blast-furnace slag cement (B, Ube-Mitsubishi Cement Corp., density 3.05 g/cm^3, JIS R5211 (JIS 2003), Chemical component: SiO_2 25.29%, Al_2O_3 8.46%, Fe_2O_3 1.92%, CaO 55.81%, MgO 3.02%, SO_3 2.04%, Na_2O 0.25%, K_2O 0.39%, TiO_2 0.43%, P_2O_5 0.12%, MnO 0.05% and Cl 0.003%, ignition loss 1.51%, insoluble 0.21%), fine sand aggregate (S, density 2.58 g/cm^3, fineness modulus 2.69), coarse aggregate (G, crushed rocks, density 2.68 g/cm^3, solid content 60 vol%), sea bottom sediments treated with HBS (water content 60 wt%, density 1.34 g/cm^3, solid particle density 2.69 g/cm^3) and additive agents (antiforming agent AFK–2, water-reducing agents EX–50 and SSP–104, Takemoto Oil & Fat Co., Ltd.). The mix proportions of the raw materials are shown in Table 4-1. Each volume for the raw material components such as cement, sand aggregate, coarse aggregate, water and sediments was changed and adjusted, in order to make their total (sum) volumes 990 dm^3/m^3. The following mixing procedures were selected. For Sample No. 1: the additive agents were added to the running water, and the cement and the fine sand aggregate were mixed with the water for 30 sec, then crushed rocks were mixed in for 90 sec. For Samples No. 2, 3, 4: a method similar to No. 1 was used, except that the cement, fine sand aggregate and sea bottom sediments were mixed with the water for 30 sec. For Sample No. 5: the cement, coarse aggregate and sea sediments were first mixed for 30 sec, then additive agents were added and finally these materials were mixed for 180 sec. For Sample No. 6: the first step was the same as for No. 5, and the water-reducing agent EX–50 was added, followed by mixing for 120 sec. Finally, the additive agent SSP–104 was added to the products. The mixing process was performed with a turbo mixer (TM–55, Pacific Machinery & Engineering Co., Ltd.). The temperature was controlled to a constant 293 K in the environmental room.

4-3-3 Evaluation of Concrete Products

The slump JIS A 1101 (JIS, 2005a), air content JIS A 1128 (JIS, 2005b), compressive strength JIS A 1108 (JIS, 2005c), total shrinkage JIS A 1129 (JIS, 2005d), and change of mass were checked for the mechanical evaluation of the concrete products (100 × 100 × 400 mm). The surface morphology of the concrete products was analyzed by scanning electron microscopy (SEM, Hitachi S-4000, Japan).

4-4 RESULTS AND DISCUSSION

4-4-1 Sediments as a Substitute for Fine Sand

The sea bottom sediments were used as the substitute for fine sand aggregate in this work. Fig. 4-1 illustrates the grain size distribution of the original sediments and the sediments treated with HBS. It also shows the recommended gradation curves of fine sand aggregates for concrete mixes according to the normal Japanese standard. The gradation of the sediments used falls within the specified gradation limits for fine aggregates.

First, a large variety of mix proportions of raw materials were investigated for the fabrication of concrete products. As a consequence, the useful volume of coarse aggregates was estimated on the basis of the selected bulk volume and solid content (60 vol%) and the volumes for the fine sand aggregates and the sediments were then determined from the difference between the total volume (990 dm^3/m^3) and the sum of the cement, coarse aggregate and water volumes. Finally,

five types of raw material components were selected for fabricating the concrete products with sea bottom sediments, as shown in Table 4-1. The sand-total aggregate ratios by volume for these mix components are presented in Table 4-2. In the equation in Table 4-2, a coefficient 0.199 was obtained from the calculation of $1.34\times0.4/2.69$. Since the raw concrete materials in Sample No. 6 could not be mixed with the mixer device, it was not possible to use this mix to fabricate a solid product.

4-4-2 Fresh Concrete Products

Slump and air content tests were conducted for the fresh concrete products. The results are presented in Table 4-3. While the slump was 72 mm in the absence of the sediments (Sample No. 1), it was in the range of 55 to 90 mm in the presence of sediments (Samples No. 2 to 5) and no significant change in the slump was observed when the sediments were used as a substitute for fine sand. The air content in samples with added sediments, except for Sample No. 5, was very similar to that of Sample No. 1.

4-4-3 Mass Loss and Total Shrinkage

The mass changes of the concrete products over time were investigated. As shown in Fig. 4-2, all of the samples that lost mass began to lose mass immediately after the construction of the fresh concrete products. The masses of the concrete Samples No. 1, 2 and 4 remained almost constant or decreased very slightly after 56 days. On the other hand, the mass of Sample No. 5 (w/c: 1.15) decreased greatly with time, owing to the evaporation of water from the materials. Here, we define α as the ratio of the mass loss of the concrete materials with the sediments to the mass loss of the normal concrete (Sample No. 1). Although the α value was nearly constant for the concrete materials containing the sediments with w/c = 0.47 and 0.69, it increased when the w/c = 1.14. The results for the total shrinkages of the concrete materials over time are depicted in Fig. 4-3. The total shrinkage includes both drying and autogenous types. The trends for the total shrinkages were almost the same as those observed in the mass change test. Here, β is defined as the ratio of the total shrinkage of the concrete materials with the sediments to the total shrinkage of the normal concrete, similar to the α value. The β values were fairly similar to the α values. Generally, the water content has a significant influence on the mass loss and shrinkage. The conventional concrete mixtures are typically prepared with water/cement ratios of 0.4–0.7 (Al-Oraimi et al., 2006). Hence, it can be concluded that if the mix proportions of raw materials are optimized, with the ratio of water to cement less than 0.7 by weight, the tendencies of mass change and shrinkage in the materials with the sediments become almost similar to those obtained with normal concrete materials.

4-4-4 Compressive Strength

The concrete blocks were tested for compressive strength after 3, 7, 28 and 187 days of curing. The effects of the ratio of water to cement on the compressive strength of the concrete materials with sediments are illustrated in Fig. 4-4, which also shows the compressive strengths of the normal concrete products for comparison purposes. After a curing age of 3 to 28 days, the compressive strengths of the concrete materials with the sediments are better than those of the normal concrete blocks. This interesting phenomenon may be attributed to chlorides in the sediments, which did not prevent the solidification/stabilization processes such as the hydration reaction and ettringite formation with the pozzolanic reaction. The compressive strengths increased with the curing time until 28 days. With an increasing w/c ratio, the compressive strengths of the concrete products with the sediments decreased. The line slopes of compressive strengths for the concrete materials with the added sediments were smaller than those of normal concrete. These facts mean that when the sediments are used as raw materials the formation of concrete with a water/cement ratio of more than one is possible, while conventional concrete mixtures are typically prepared with a w/c ratio from 0.4 to 0.7. After 28 days of curing, the compressive strength was 43 MPa for the concrete products with w/c = 0.47 that used the sediments. After 187 days, the compressive strengths of the concrete blocks with the sediments were 44, 31 and 12 MPa with w/c = 0.47, 0.69 and 1.15, respectively.

4-4-5 Surface Morphology

To check the microstructure of the surface of the concrete products, the surface morphology was evaluated by scanning electron microscopy (SEM). The results are illustrated in Fig. 4-5. Ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) occurs in the concrete in various forms, often as spherical clusters of ettringite crystals, felt-like or parallel needles of different sizes (Stark et al., 2000). If the ettringite crystallizes out without spatial obstruction, e.g. in pores, it has the typical needle-shaped crystal habit. The needle-shaped ettringite was observed only in Sample No. 5 with w/c = 1.15. The compressive strengths of the concrete products decreased with an increase in the w/c ratio. Therefore, we can conclude that the ettringite formed a three-dimensional network structure in the early stages of hydration (within 7 days) and the next solidification/stabilization processes occurred after the ettringite formation, with the pozzolanic reaction in the samples with a w/c of less than 0.69. Shrinkage cracks were observed in the surface of concrete product No. 5. This phenomenon could be attributed to significant mass loss and shrinkage on the basis of the data from Figs. 4-2 and 4-3. No shrinkage cracks occurred after 187 days of curing on the surface of the other samples.

4-4-6 Application in the field

We field-tested the concrete product with w/c = 0.47 made with sea bottom sediments for constructing marine reefs. First, a rectangular parallel shape (100 × 100 × 400 mm) of the concrete product was prepared and deployed in the sea after curing 187 days, as depicted in Fig. 4-6 (a). After approximately one year of deployment in the field, no damage was noticed as a result of the sea environmental changes. The observed compressive strengths were 48, 33 and 14 MPa for w/c ratios of 0.47, 0.69 and 1.15, respectively (Table 4-4). The change in the shrinkage might be attributed to the expansion due to the absorption of water. These results suggested that the concrete block contains sea bottom sediments has enough stability to be sued for marine applications. Based on this encouraged data a scaled-up size of the concrete product (1700 × 1300 × 650 mm) to be used as a large marine reef was fabricated as shown in Fig. 4-7 (b). No steel reinforcement was added to the concrete. The application of the scaled-up size of the concrete product in the field is still being examined.

4-5 CONCLUSION

The use of sea sediments as a substitute for fine sand aggregate was investigated for the fabrication of concrete solids and marine reefs. The composition of the raw materials was optimized, and the different concrete materials were assessed by testing their slump, air content, mass change, total shrinkage and compressive strength. After 187 days of curing, the compressive strength was 44 MPa for the concrete products with w/c = 0.47 using the sediments. Furthermore, after immersing in the sea environment during approximately one year, the compressive strengths were 48, 33 and 14 MPa for the concretes with w/c = 0.47, 0.69 and 1.15, respectively. These results indicated that the concrete blocks with the sea bottom sediments which were continuously field-tested in the real sea environment for 1 year did not receive any damage from the sea.

Table 4-1. Raw materials for the concrete blocks.

No.	Raw material components(kg/m^3)									Additive agents(cm^3/m^3)		
	C[a]	Sediments	Water added	S[b]	G[c]	Total	Water in Sediments[d]	Total Water[e]	W/C[f]	AFK-2	EX-50	SSP-104
1	420	0	168	759	1045	2392	0	168	0.40	2.8	552	-
2	420	50	168	640	1069	2347	30	198	0.47	2.8	552	-
3	420	100	168	519	1093	2300	60	198	0.53	2.8	552	-
4	420	200	168	248	1174	2210	120	288	0.69	3.3	656	-
5	500	954	0	0	300	1754	572	572	1.14	8.2	1640	-
6	500	1054	0	0	100	1654	632	632	1.26	0	1640	820

[a] cement, [b] fine sand aggregate, [c] coarse aggregate(crushed rocks), [d] water content 60% wt% in sediments, [e] sum of water added and water contained in sediments.

[f] ratio of water to cement by weight.

Table 4-2.　Bulk volume of the coarse aggregate and the sand-total aggregate ratios.

No.	G[a]		S[b]	Sediments(Z)	S/a[c]
	Volume (dm^3/m^3)	Bulk volume (m^3/m^3)	(dm^3/m^3)	(dm^3/m^3)	(m^3/m^3)
1	390	0.650	294	0	0.43
2	399	0.665	248	37	0.39
3	408	0.680	201	75	0.35
4	438	0.730	96	150	0.22
5	112	0.180	0	714	0.56
6	37	0.600	0	791	0.81

[a] coarse aggregate(crushed rocks), [b] fine sand aggregate, [c] sand-total aggregate ratio by volume.

S/a was calculated from the following equation:

$$S/a = \frac{S + 0.199Z}{G + S + 0.199Z}$$

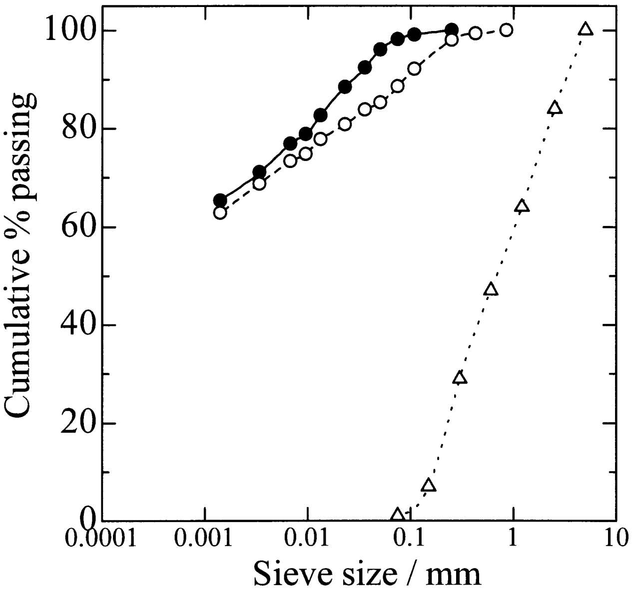

Figure 4-1: Gradation curves for the original sediments (●), sediments treated with HBS (○) and the fine sand aggregates for the concrete mixes according to the normal Japanese standard (△).

Table 4-3. Slump and air content of the fresh concrete products.

No.	**Slump (mm)**	**Air content (%)**
1	**72**	**1.5**
2	**70**	**1.7**
3	**90**	**1.5**
4	**79**	**1.3**
5	**55**	**3.5**

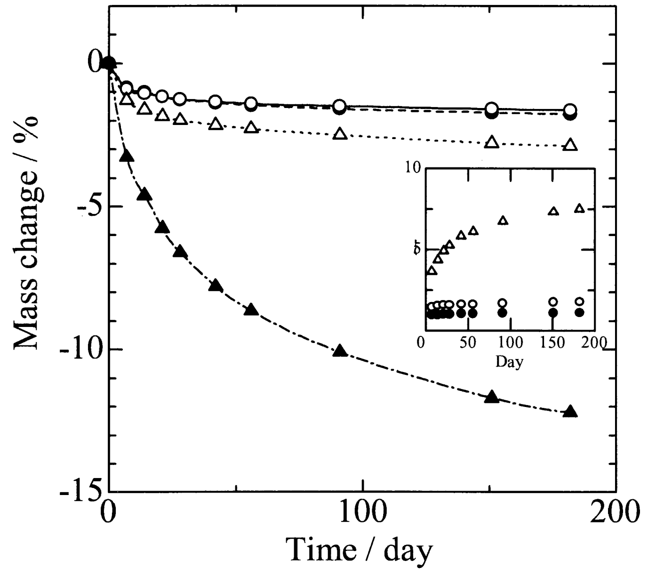

Figure 4-2. Effect of the water/cement ratio on the mass changes of the concrete products. ○; Sample No. 1 with w/c 0.40, ●; Sample No. 2 with w/c 0.47, △; Sample No. 4 with w/c 0.69 and ▲; Sample No. 5 with w/c 1.15. The insert figure shows α versus the curing age. α was defined as the ratio of mass loss of the concrete materials with the sediments to the mass loss of the normal concrete (sample No. 1). In the insert figure, ●; Sample No. 2, ○; Sample No. 4 and △; Sample No. 5.

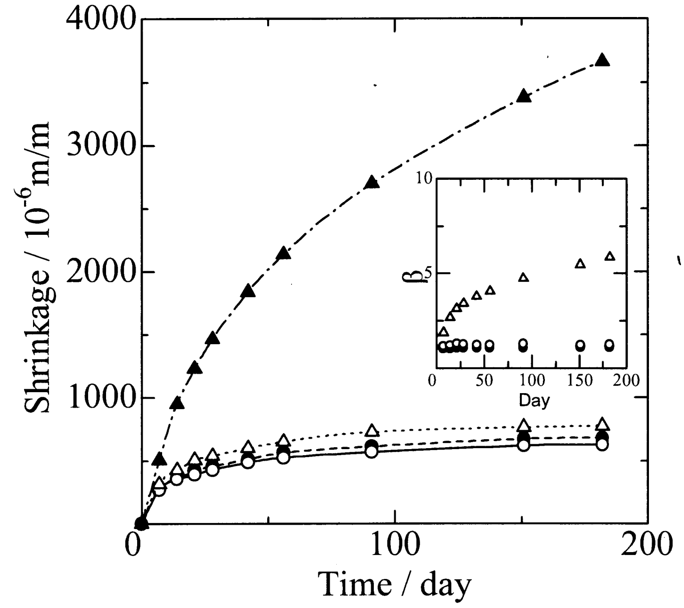

Figure 4-3. Effect of the water/cement ratio on the total shrinkage of the concrete products. ○; Sample No. 1 with w/c 0.40, ●; Sample No. 2 with w/c 0.47, △; Sample No. 4 with w/c 0.69 and ▲; Sample No. 5 with w/c 1.15. The insert figure shows β versus the curing age. β was defined as the ratio of the total shrinkage of the concrete materials with the sediments to the total shrinkage of the normal concrete (Sample No. 1). In the insert figure, ●; Sample No. 2, ○; Sample No. 4 and △; Sample No. 5.

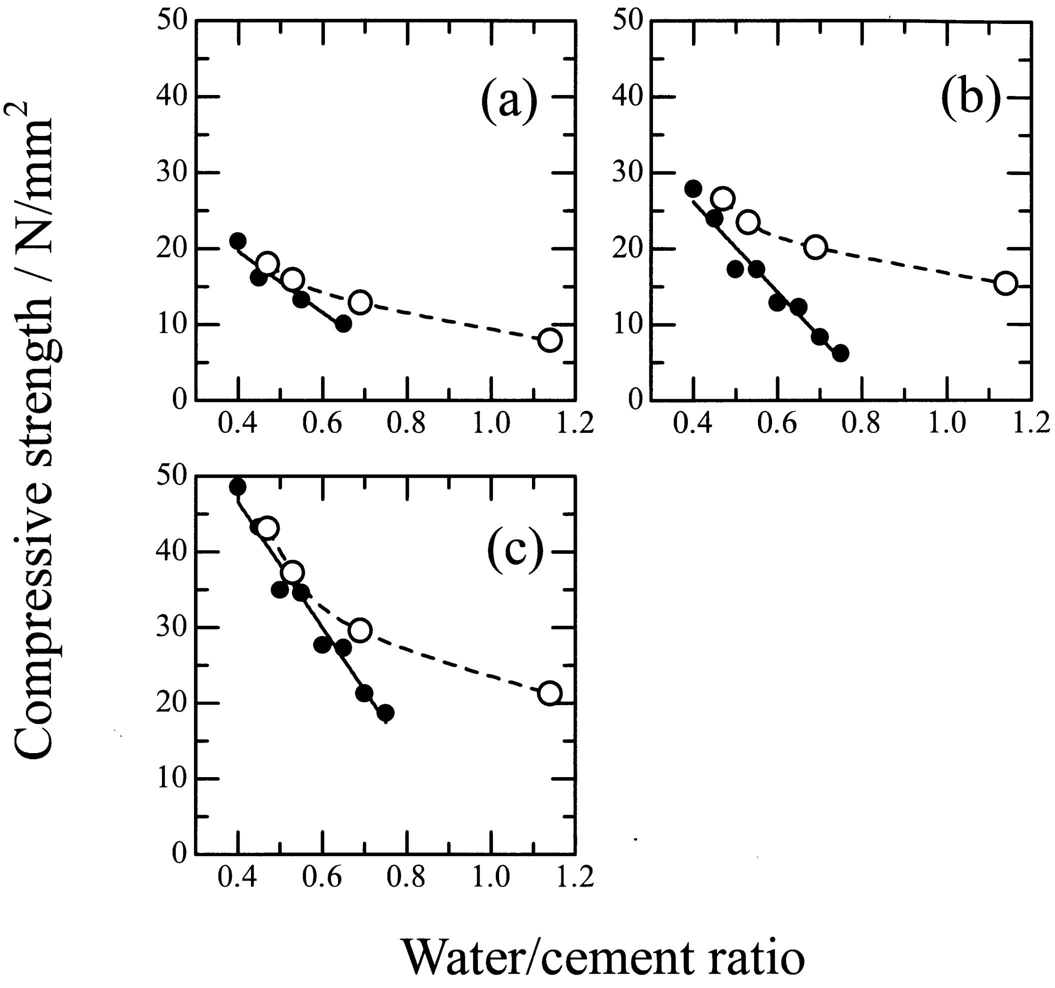

Figure 4-4. Effect of the ratio of water to cement on the compressive strength of the concrete products. ○; concrete materials with the sediments, ●; normal concrete products. Curing age; (a) 3, (b) 7, and (c) 28 days.

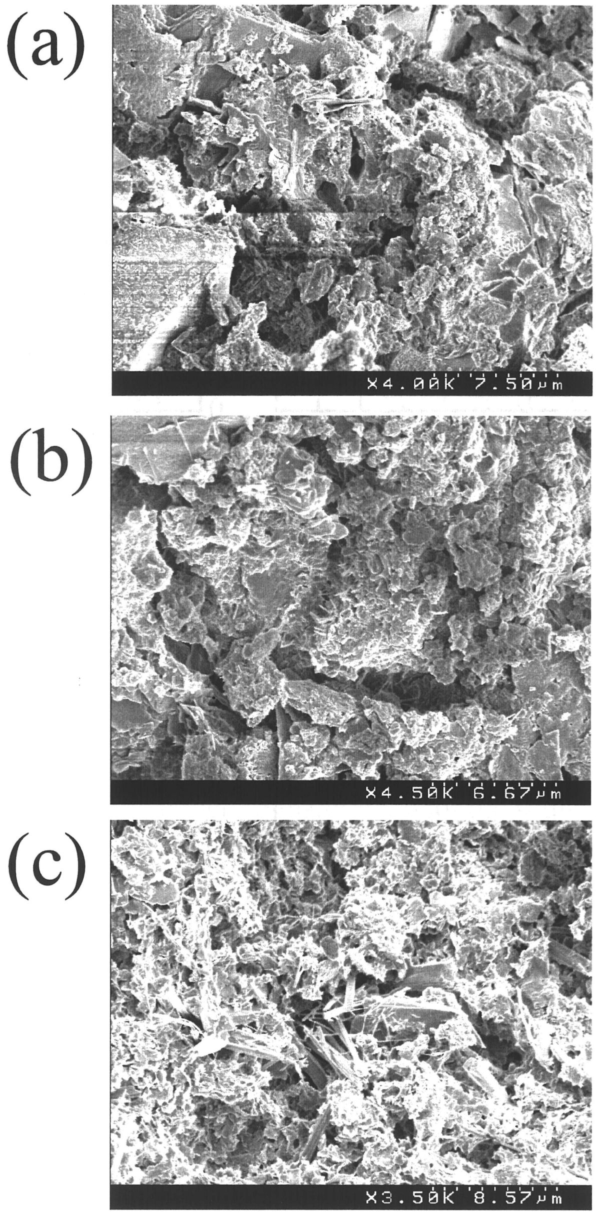

Figure 4-5. Scanning electron microscopic picture of the microstructure of the sample surface with a curing age of 7 days. (a) Sample No.1, (b); No.2, and (c); No.5.

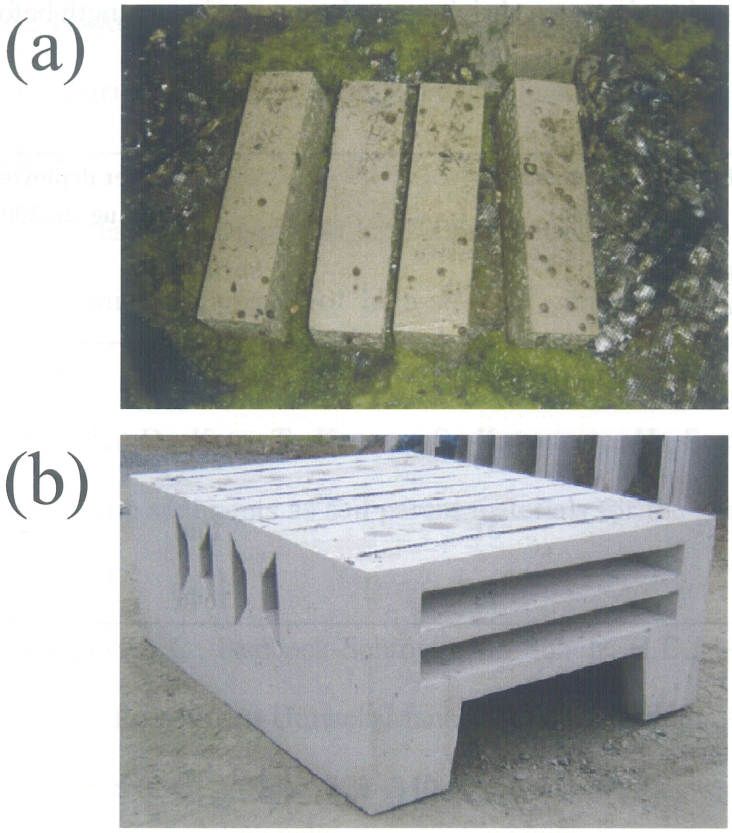

Figure 4-6. (a) Immersion of the concrete product in the sea. (b) Scaled-up size of concrete products for marine reefs.

Table 4-4. Comparison between shrinkage and compressive strength before and after deployment in the sea.

	Before deployment (Sep. 20/2006)		**After deployment (Aug. 28/2007)**	
No.	**Shrinkage (10^{-6} m/m)**	**Compressive strength (N/mm^2)**	**Shrinkage (10^{-6} m/m)**	**Compressive strength (N/mm^2)**
1	635	51	248	60
2	680	44	215	48
4	718	31	100	33
5	3656	12	1646	14

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CHAPTER 5 DEGRADATION OF MARINE HUMIC ACIDS BY OZONE-INITIATED RADICAL REACTIONS

5-1 ABSTRACT

Degradation of humic acids extracted from seabed sediment collected from two different locations in Japan was carried out using an ozone treatment technique. Degradation was evaluated by UV_{254}/VIS_{400} absorbance, high performance size exclusion chromatography (HPSEC) and total organic carbon (TOC). Sediment was collected from Ago Bay, Mie prefecture and Ariake Bay, Fukuoka prefecture, Japan. After the ozone treatment, a decrease in absorbance of humic acids was observed over a wide range of pH. The UV_{254} absorbance of all humic acids showed a significant decrease. Furthermore, under neutral pH, more than 80% degradation was achieved for both sediments, with an initial humic acid concentration of 30 mg L^{-1}. The total organic carbon (TOC) content of ozone-dosed solutions showed no significant changes. The decrease in the molecular weight of humic acids was evaluated using the values obtained by high performance size exclusion chromatographic (HPSEC) analysis. The decrease in the value of humic acids in extracted solutions was related to the key materials in the sediment, which result from the semi-closed sea environment. Significant environmental improvement can be expected from the use of this technology.

5-2 INTRODUCTION

Removal of organic substances that have accumulated due to aquacultural and other industrial purposes in seabed sediments is of great importance in environmental protection. In Ago Bay, Japan, more than 10% (by weight) of the sediment is composed of organic substances. Furthermore, humic substances represent between 37% and 51% of these organic substances (Kaneco et al. 2005). Humic substances are not well defined, but are generally divided into three fractions: humin, which represents the insoluble components in aqueous solution at all pH values; humic acids (HA), which are soluble in alkaline to weakly acidic solutions, but deposit at or below pH 2.0; and fulvic acids (FA), which are soluble in aqueous solutions at all pH values (Thurman et al., 1982; Mansuy et al., 2001; Kawahigashi et al., 2005; Rozenbaha et al., 2002). Humic substances, some of which occur naturally, are a useful source of organic matter and improve fertilization levels in agricultural soils and the physico-chemical properties of the soil when used in land restoration. The characteristics of humic acids extracted from sewage sludge-amended oxisols have been investigated using electron paramagnetic resonance (Perez et al., 2006). In recent years, humic acids from different environmental areas have been characterized (Kang et al., 2002). In marine ecology, the increased supply of organic matter in seabed sediments causes a phenomenon named eutrophication. As a result, so-called "red tides", which occur most frequently in summer, have been become a widely recognized problem in coastal areas, and many efforts have been made to combat this problem.

Several techniques have been developed in the field of water purification that use UV-radiation and/or ozonation for the degradation of organic pollutants, which provide high formation rates of hydroxyl radicals. Many studies using ozonation have been carried out with established techniques for the degradation of pollutants in municipal wastewaters, industrial wastewaters, and landfill leachates (Arai et al., 1986; Gulyas et al., 1995; Beschkov et al., 1997; Cho et al., 2003; Latifoglu and Gurol, 2003, Kusic et al., 2006). The effects of humic substances have become of increasing importance in water treatment because they may interact with the chemicals used through catalytic reactions, sorption, solubilization, photosensitization and quenching (Karnik et al., 2005). In the removal of organic substances in water by ozonation processes, an understanding of the effect of humic substances on the degradation reaction is important in devising effective treatments. Previous studies on the ozone consumption of humic substances during the ozonation process have indicated that humic substances are radical scavengers (Staehelin and Hoigne, 1985). However, the reaction of ozone with humic substances might also generate species that promote the conversion of O_3 into OH• (Staehelin and Hoigne, 1985; Xiong et al., 1992). To our knowledge, there have been few studies of the degradation of humic acids using ozonation (Ohlenbusch et al., 1998; Kerc et al., 2003). In particular, despite the fact that the contamination of seabed sediments with organic substances causes serious problems for the environment, the effects of humic substances for the removal of organic pollutants by these processes have not been investigated and compared in detail by analysis of the reaction mechanisms.

The purpose of the present paper is to report a study of degradation by the ozonation technique of humic substances in seabed sediments collected from two different locations in Japan (Ago Bay and Ariake Bay). The experimental data were compared with data obtained using the commercial Aldrich humic acid which was isolated from coal. The degradation process was monitored using a UV/VIS spectrophotometer and total organic carbon (TOC) analyzer. In addition, changes in the molecular weight distribution of HA were clarified by high performance size exclusion chromatography (HPSEC).

5-3 EXPERIMENTAL METHODS

5-3-1 Humic acid samples

The HA sample was purchased from Aldrich and was used as received. The chemical information of Aldrich humic acid has been reported as follows: weight- averaged molecular weight; 4100, number-averaged molecular weight; 1630, M_w/M_n; 2.5, polydispersity (ε); 919 L^{-1} (mole of OC) $^{-1}$ cm $^{-1}$, the ratio of absorbance (465 nm) to absorbance (665 nm); 7.59. HA (300 mg L^{-1}).was dissolved in 0.1 M NaOH. For experimental use, the pH of the humic acid solution was adjusted using 1 M HCl. All aqueous solutions were prepared with ultrapure water obtained from an ultrapure water system (Advantec MFS Inc., Tokyo, Japan), resulting in a resistivity > 18 MΩ cm. All chemicals and solvents in this work were of the purest grade commercially available.

For the environmental study, soil samples were collected from Tategami in Ago Bay (S1) and Kumata in Ariake Bay (S2), Japan, as shown in Fig. 5-1. A modified process was used to extract humic acids (Kaneco et al., 2005). The sediments collected from the study sites were sieved through a 2 mm mesh in order to remove the large extraneous particles such as bivalve shells and other waste. The samples were then dried at 105°C for 1 day in an electric oven. After drying, the humic acids contained in 50 g of each sediment sample were extracted with 500 ml of 1M NaOH at 90°C for 4 hrs on a hot plate. The humic acid solutions were separated from the sediment using a glass fiber filter (Advantec Inc, Tokyo, Japan), then adjusted to the required pH with 1 M HCl and diluted to the required concentration to perform the study.

5-3-2 Ozonation of humic acids

A schematic diagram of the experimental system is shown in Fig. 5-2. The ozone was produced from dry oxygen gas using an ozonator (Eco-desine Co. Ltd., Model ED-OG-R4), with settings of 0.1 MPa, an ozone flow rate of 1 L min^{-1}, an electric current of 1 A, and an ozone concentration of 10 wt% in a 200 ml reaction solution. In the ozonation system, outlet flows were trapped with a potassium iodide solution to prevent any leakage.

The humic acids, at a concentration of 30 mg L^{-1}, adjusted to pH values of 4, 7 and 12, were ozonated. Following this, different concentrations of the Aldrich HA and the marine humic acids, adjusted to pH 7, were treated. After ozonation, samples were measured by spectrophotometry to characterize the degradation of marine humic acids.

5-3-3 Evaluation of the humic acid degradation

The effects of ozonation were determined using a UV/VIS spectrophotometer (Shimadzu Co.

Ltd). Two different wavelengths were evaluated: UV_{254} was used for aromatic compounds, whereas color was evaluated by the absorbance at VIS_{400}. The degradation rate was calculated using the following equation,

$$\frac{C}{C_0} = \frac{UV_{254(t)}}{UV_{254(0)}} \qquad (1)$$

where $UV_{254(0)}$ and $UV_{254(t)}$ are the absorbance at the 254 nm wavelength at the initial time and the reaction time, respectively.

The molecular weight distributions of Aldrich HA and the marine humic acids were evaluated using a high-performance size-exclusion chromatography (HPSEC) system, which comprised a TRI ROTER-V JASCO solvent pump, a UVIDEC-100-V1 JASCO variable wavelength absorbance detector, a TU-100 JASCO thermostat, and a Rheodyne rotary injector valve with a 20 μl·sample loop. A Shodex 805HQ (0.75 cm in diameter, 30 cm in height, Showa Denko KK, Tokyo, Japan) preceded by a guard column was used for separation by size exclusion. The applied flow rate was 1.0 ml min^{-1}. The column packing material (a polymerized diol covalently bonded to a silica support, exclusion limit 4,000,000, permeation limit 100) was selected based upon its low residual hydrophobicity and minimal ion-exchange capacity (Wang et al., 1997). The mobile phase consisted of 0.01 M K_2HPO_4–0.01 M KH_2PO_4 solutions buffered to pH 7.0. The HPSEC system was calibrated using pullulan (Shodex STANDARD p-82).

The TOC in the ozonated solutions was measured using a TOC analyzer (TOC-V CPH, TNM-1, SHIMADZU). The ignition loss (IL), total organic carbon (TOC) and total nitrogen (T-N) in the sediments from two places were measured before and after the extraction of humic acids. The IL was measured as the difference in weight between dried (100°C for 1 hour) and combusted (600°C for 30 min) sediments (JIS, 1998). An electric oven (Koyo Box Furnace, KBF828N, Nara, Japan) was used for the combustion. The TOC and T-N were measured using a

CN corder (VARIO MAX CHS, GmbH) on the dry sediments after treatment with 1 N HCl to remove the calcium carbonate derived from bivalves.

5-4 RESULTS AND DISCUSSION

5-4-1 Degradation of Aldrich humic acid

To clarify the degradation characteristics of HA as a result of ozone treatment, spectroscopic data for the ozonated Aldrich HA were compared with data obtained for HA before reaction. The UV-VIS absorption spectrum of HA exhibited the same pattern as found in a previous study with the Fenton reaction (Katsumata et al., 2007). As shown in Fig. 5-3, the absorbance at 220–420 nm decreased with increased reaction time as a result of the ozonation process. Consequently, it was confirmed that the ozonation process is an effective technique for the decomposition of humic acid.

Fig. 5-3 shows that the specific visible absorbance VIS_{400} was completely removed after a reaction time of 15 min, as can also be identified clearly in Fig. 5-4. However, the absorbance of aromatic moieties at UV_{254} was still present after 15 min. Despite increasing the ozone reaction time to 60 min, no remarkable change in the decomposition of UV_{254} was apparent. Although ozonation for 1 minute was followed by a change in ozone concentration from 0.5 L min^{-1} to 3 L min^{-1}, the difference was not significant.

The pH value of a solution is an important parameter in wastewater treatment. The effect of pH on the decomposition of the Aldrich HA was investigated in this study over a pH range from 4 to 12 without the addition of buffer solution. Fig. 5-5 shows the change in concentration of the Aldrich HA as a function of the reaction time. After 15 min, 71.6, 87.7 and 96.1% of the Aldrich HA had been removed at pH 4, 7 and 12, respectively. Thus, larger decomposition was observed at the higher pH after 15 min. This phenomenon was attributed to the effects of the OH• radical in the work of Alkality (Qi et al., 2004). Furthermore, a decrease in the pH of the reaction solution was observed during the pH 7 ozonation. Therefore, these results can be explained by a decrease in molecular size due to the formation of formic acid and oxalic acid by the decomposition of humic acid (Kerc et al., 2003; Qi et al., 2004).

The effect of initial HA concentration was studied using Aldrich HA at a range of concentrations from 15 mg L^{-1} to 150 mg L^{-1} at pH 7 (Fig. 5-6). After 15 min, 88.9, 87.7, 81.0 and 77.8 % of the HA (resulting in concentrations of 13.3, 26.3, 60.7 and 116.7 mg L^{-1}, respectively) were removed at original concentrations of 15, 30, 75 and 150 mg L^{-1}, respectively. The degradation of HA has also been explained using a pseudo-first order degradation equation model (Bekbolet et al., 1998). The degradation rate constant (min^{-1}) is represented as k_{oz} for ozone oxidation in the following equation.

$$\frac{d[HA]}{dt} = -k_{oz}[HA] \qquad (2)$$

From this equation, as shown in the insert of Fig. 5-6, the decomposition rate (k_{oz}) was calculated to be 1.8×10^{-1}, 2.9×10^{-1}, 5.1×10^{-1} and 13×10^{-1} min^{-1}, for ozonation at concentrations of 150, 75, 30 and 15 mg L^{-1}, respectively. The data, obtained by the same method, on the humic acid degradation rate using ozonation, based on UV_{254} and VIS_{400} parameters, are presented in Table 5-1. The rate constants calculated in this study were higher than those reported from previous studies (Kerc et al., 2003). This can be explained by the structural differences in the humic acids used in the experiments, and by the alterations in the humic acid molecules as an effect of preozonation (Kerc et al., 2003; Gonenc and Bekbolet, 2001). Conversely, the calculated rate constant of VIS_{400} was observed to be faster than that of UV_{254}, which represents the carbon double bonds and aromatic structure within the humic acid molecule. Rapid decoloration with ozonation may be attributed to rapid attack by the ozone molecule on the chromophoric functional groups in the outer regions of the humic acid molecule. Thus, these results suggest that the humic acid dosage is correlated with the rate of decomposition of humic substances.

5-4-2 Degradation of marine humic acid

Fig. 5-7 depicts the decomposition of the marine humic acids, extracted from the Ago Bay and Ariake Bay sediments, respectively. The decomposition efficiencies reached 80% during 10 minutes' ozonation. Similar results were also obtained in a 60 min reaction time, which gave a decomposition efficiency of between 80 and 90%. Since the humic acid sample was applied into the HPSEC analysis, the results were compared with those obtained before the treatment. (Fig. 5-8). It was found from a result of the HPSEC that the ozone treatment made the molecular weight of humic acid very extremely low in an instant because the HPSEC of marine humic aicds proved the larger retention time of peak and lower peak height with increasing the treatment time. The insert in Fig. 6 shows α, which was defined as the rate of change of pH compared to the initial pH, versus the ozonation time, which also describes this phenomenon. These results suggest that the molecular weight decreased during decomposition of the humic acid.

In this study, the humic substances in the seabed sediments were able to be resolved using ozone-initiated radical reactions. In the future, these solidified sediments, following purification by ozone treatment, could be used with future advanced technology as natural ecosystem recovery materials (Kaneco et al., 2004).

5-4-3 Total organic carbon

Fig. 5-9 shows the degradation of TOC in the ozone treatment solution during a 15-min reaction. Our expectation was that TOC reduction might occur after the ozonation; however, no remarkable change in S1 and S2 was observed with the dosed solutions. In the dosed solution containing HA, the TOC decreased (a 20% decrement) over 3 min for 15 to 75 mg L^{-1} of humic acid. When the 150 mg L^{-1} initial concentration was studied, the degradation occurred later in the initial stage. After 15 min, the TOC became constant. Therefore, these results reflect that organic carbon could not be mineralized into carbon dioxide by the ozone treatment. However, the load environment of marine humic acids could be considered to be lowered with the ozone treatment, since the molecular weight of organic substances became very extremely low (Wenzel et al., 1999).

Table 5-2 shows the IL, TOC and T-N in the sediments before and after extraction with the humic substances from S1 and S2. Overall, the data for S1 were higher than those from S2. These data indicated that the organic substances were equivalent to those that are resolved rather easily: the depletion rates for IL following extraction relative to before extraction were 0.40 and 0.25 for S1 and S2, respectively. This might be attributed to a difference in the degradation efficiency, which was 30% larger for S1. As shown in Fig. 5-6 and Table 5-1, a higher degradation efficiency was generally observed for S1. In general, in Ago Bay (S1), sediments have accumulated that consist of fine particles originating from eutrophication. In contrast, the sediments from Ariake Bay (S2) accumulate in the mouth of the Chikugo River, and therefore might be consistent with an origin on land (Shirota and Tanaka, 1981). These results suggest that the organic materials originating from these organic particles were equivalent to easily resolved organic materials.

5-5 CONCLUSION

Ozonation was demonstrated to be a very efficient technique, and was able to produce a clear color in samples contaminated with marine humic acid within approximately 15 minutes. High molecular weight substances were degraded into low molecular weight substances; however, complete removal was impossible. Degradation of humic acids could be helpful in the restoration of the marine ecosystem in seabed sediments. Moreover, this technique could be used to treat other high molecular weight substances from different wastes.

Table 5-1. Degradation rate constant for different humic acid samples under ozonation treatment.

Humic acid, mg/L	Aldrich HA				TA				KA			
	UV_{254}		VIS_{400}		UV_{254}		VIS_{400}		UV_{254}		VIS_{400}	
	k_{oz}, min^{-1}	$t_{1/2}$, min	k_{oz}, min^{-1}	$t_{1/2}$, min	k_{oz}, min^{-1}	$t_{1/2}$, min	k_{oz}, min^{-1}	$t_{1/2}$, min	k_{oz}, min^{-1}	$t_{1/2}$, min	k_{oz}, min^{-1}	$t_{1/2}$, min
15	1.31	0.50	1.98	0.35	-	-	-	-	-	-	-	-
30	5.14×10^{-1}	1.3	7.38×10^{-1}	0.90	3.99×10^{-1}	1.7	9.21×10^{-1}	0.8	3.63×10^{-1}	1.9	7.13×10^{-1}	1.0
75	2.87×10^{-1}	2.4	4.36×10^{-1}	1.6	-	-	-	-	-	-	-	-
150	1.84×10^{-1}	3.8	2.94×10^{-1}	2.4	-	-	-	-	-	-	-	-

Table 5-2. The IL, TOC and T-N in the seabed sediments from Ago Bay (S1) and Ariake Bay (S2).

Sampling station		IL (%)	TOC (mg/g)	T-N (mg/g)
S1	Before [a]	11.2	38.6	3.48
	After [b]	6.7	15.5	1.50
S2	Before [a]	10.6	16.6	1.47
	After [b]	8.0	7.63	0.51

[a] Before extraction of humic acids, [b] After extraction of humic acids.

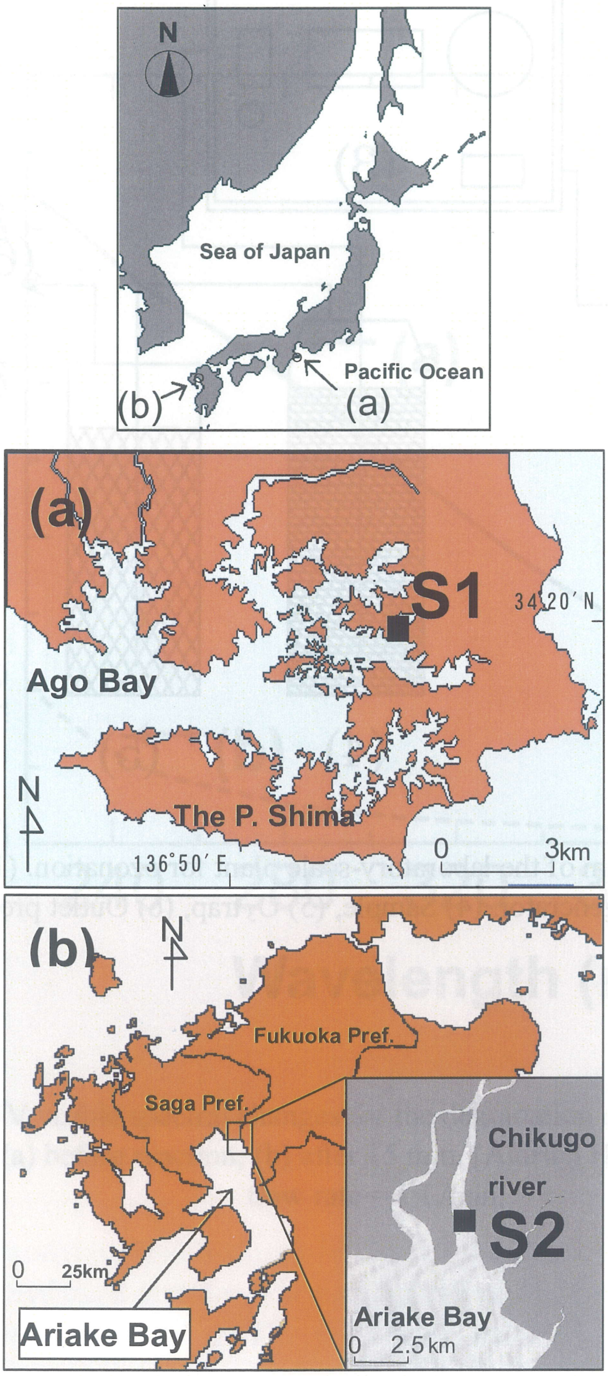

Figure 5-1. Location of (a) Ago Bay (S1) in Mie prefecture and (b) Ariake Bay (S2) in Fukuoka prefecture, Japan.

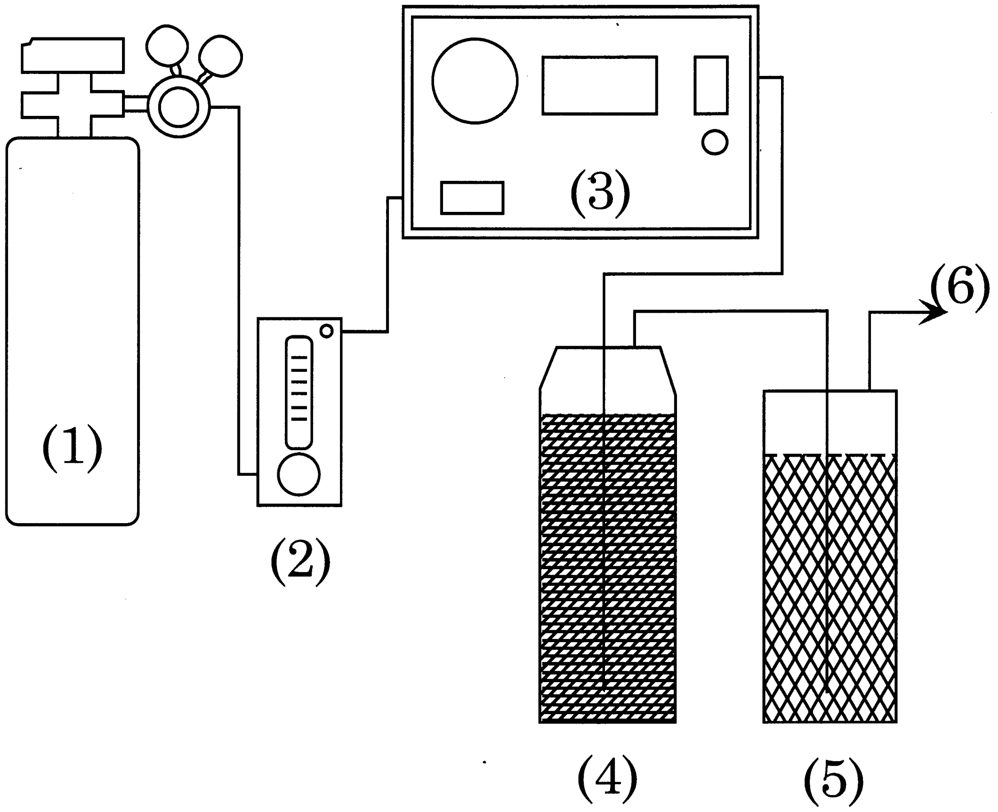

Figure 5-2. Schematic diagram of the laboratory-scale plant for ozonation. (1) O_2 gas, (2) Flow meter, (3) Ozone generator, (4) Sample, (5) O_3 trap, (6) Outlet product.

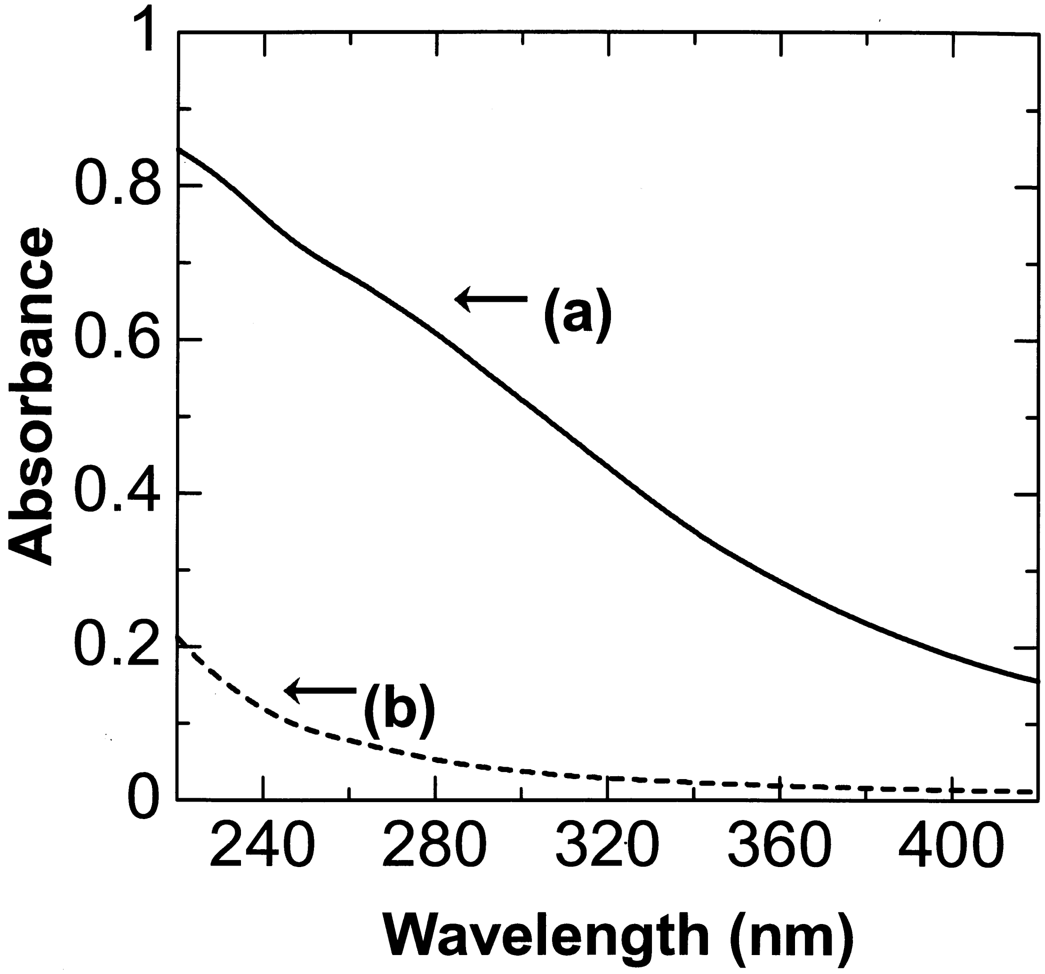

Figure 5-3. UV-visible spectral changes for the degradation of the Aldrich HA under the ozonation process. (a) before reaction; (b) after 15 min. [Aldrich HA] = 30 mg L^{-1}, O_3 = 10 wt%, flow rate = 1 L/min.

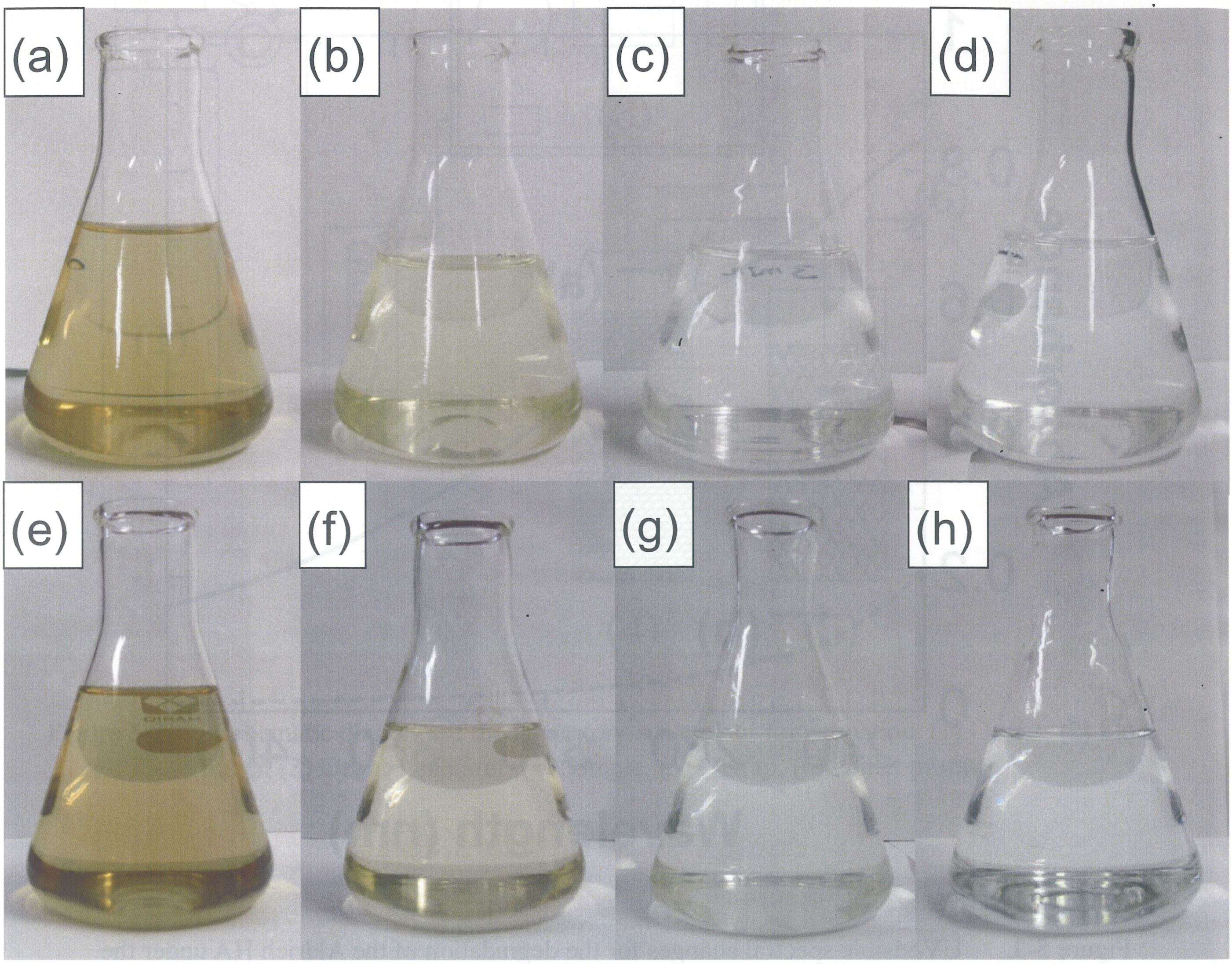

Figure 5-4. Photographs of the Aldrich HA and S1 during ozonation treatments: a, b, c and d are Aldrich HA; e, f, g and h are S1 (Ago Bay); from a to d, and e to h are before reaction, 1 min, 3min and 15 min, respectively. [Aldrich HA and S1] = 30 mg L^{-1}, O_3 = 10 wt%, flow rate = 1 L/min, pH = 7.

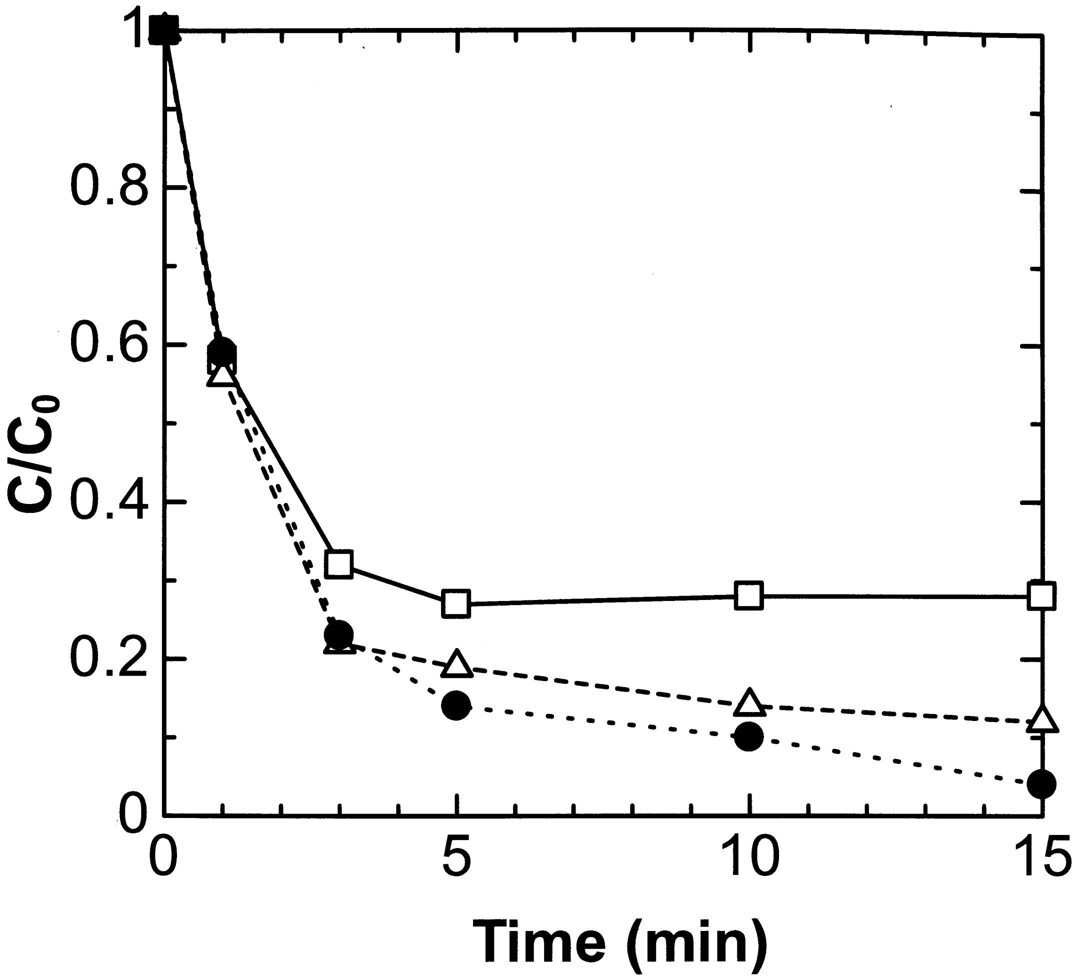

Figure 5-5. Degradation of the Aldrich HA at different pH values. [Aldrich HA] = 30 mg L^{-1}, O_3 = 10 wt%, flow rate = 1 L/min. Rectangular: pH = 4, Triangles: pH = 7, Solid circles: pH = 12.

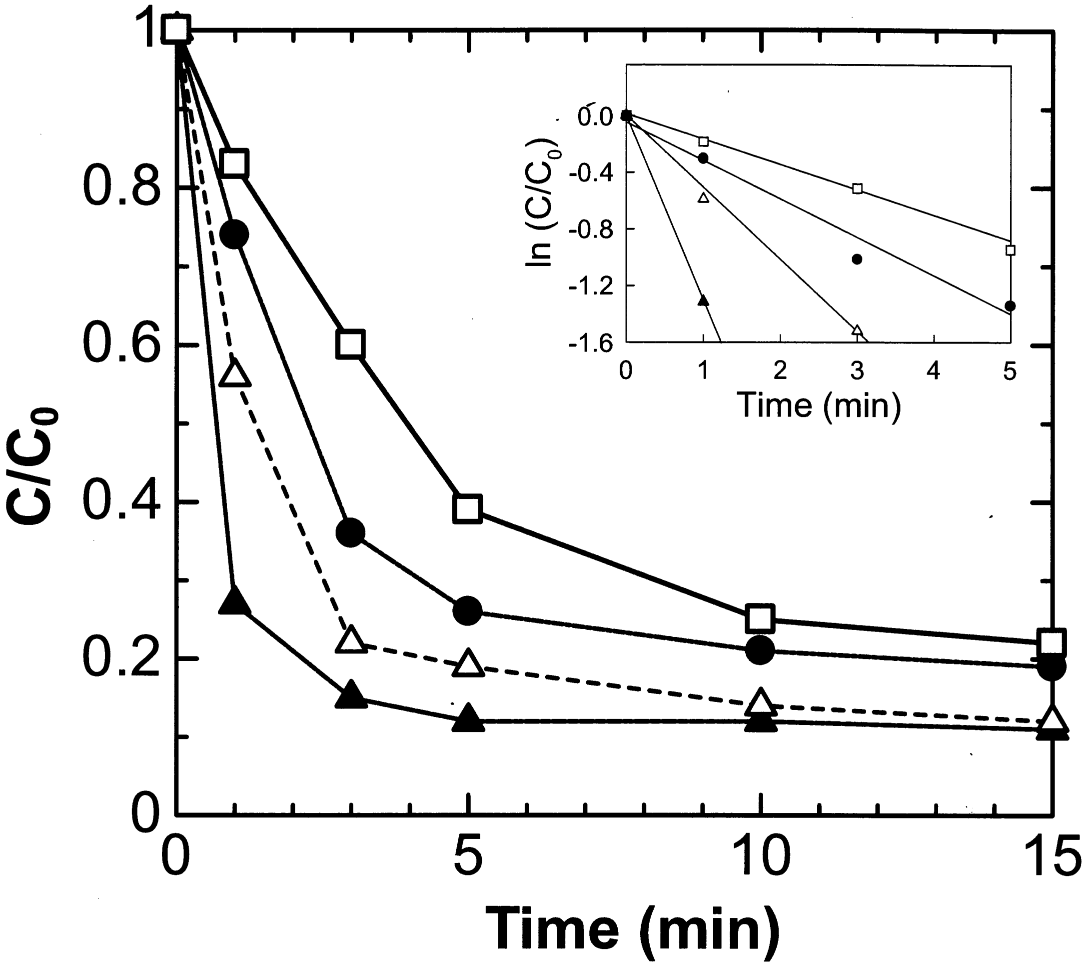

Figure 5-6. Degradation of the Aldrich HA at different concentrations. O_3 = 10 wt%, flow rate = 1 L/min, pH = 7. Rectangular: 150 mg L^{-1}, Solid circles: 75 mg L^{-1}, Open triangles: 30 mg L^{-1}, Solid triangles: 15 mg L^{-1}. The insert figure shows ln(C/C_0) versus the ozonation time.

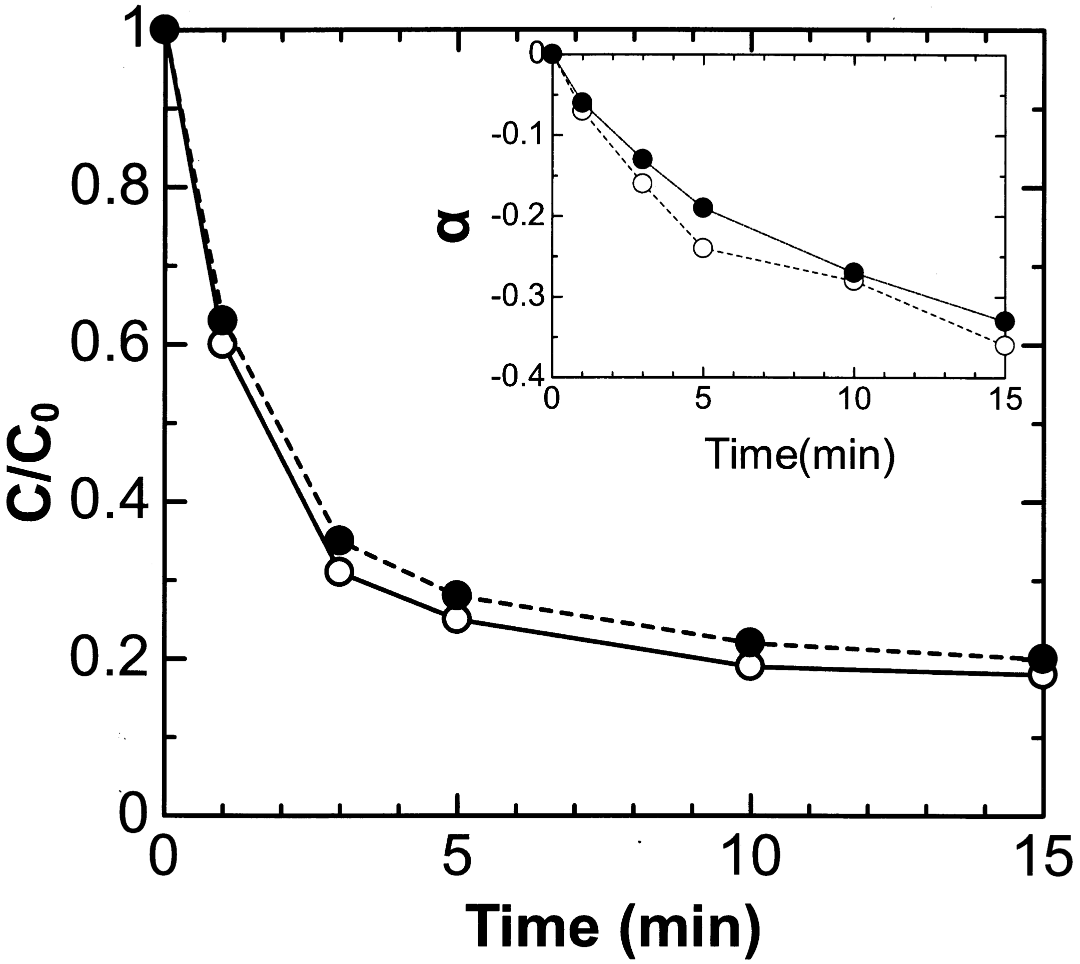

Figure 5-7. Degradation of S1 (Ago Bay) and S2 (Ariake Bay). [S1] = 30 mg L^{-1}, [S2] = 30 mg L^{-1}, O_3 = 10 wt%, flow rate = 1 L/min, pH = 7. Open circles: Ago Bay, Solid circles: Ariake Bay. The insert figure shows α versus the ozonation time. The α was defined as the rate of change of pH compared with the initial pH.

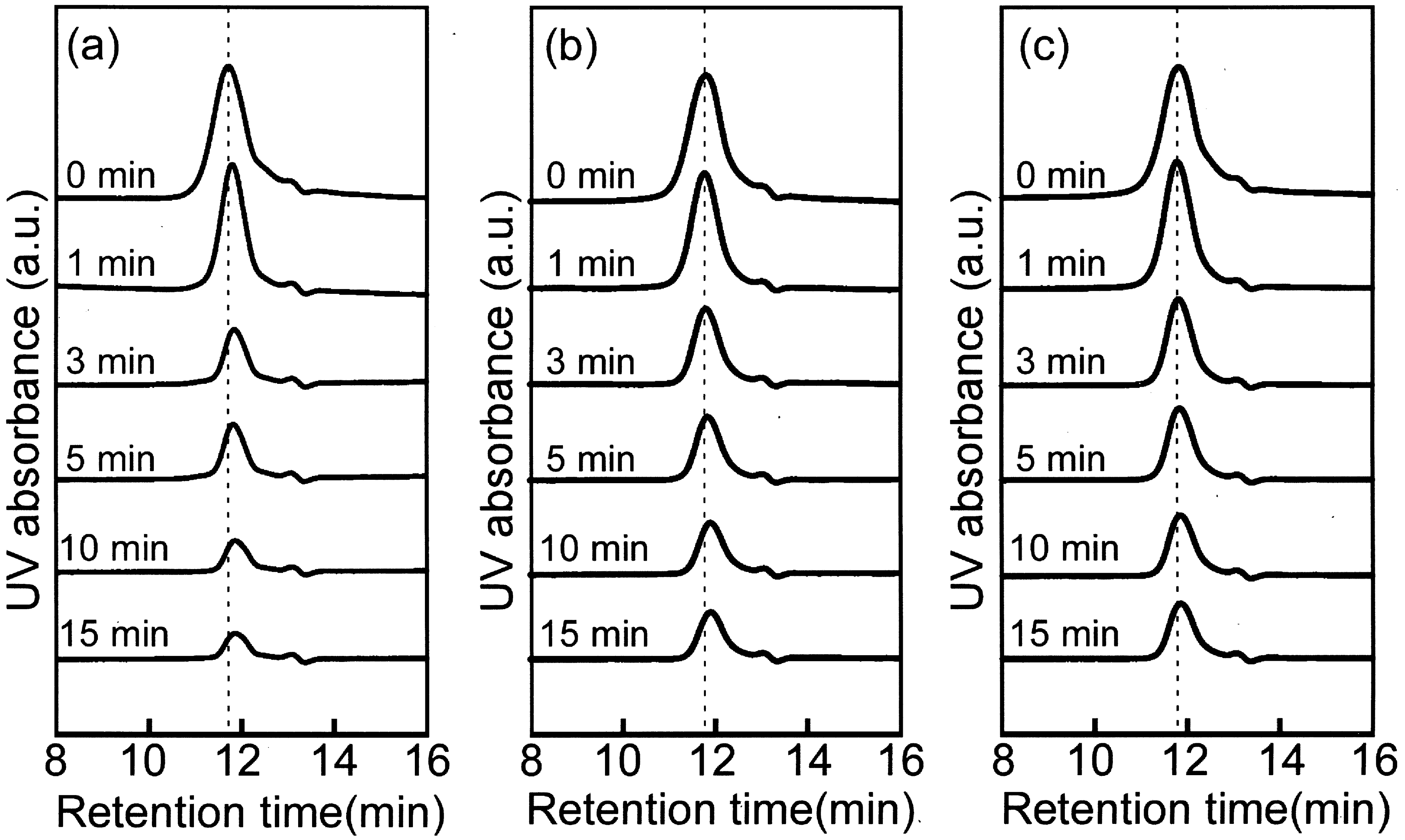

Figure 5-8. Analysis of HPSEC chromatograms under ozonation. (a) Aldrich HA, (b) S1, (c) S2. [Aldrich HA, S1 and S2] = 30 mg L^{-1}, O_3 = 10 wt%, flow rate = 1 L/min, pH = 7.

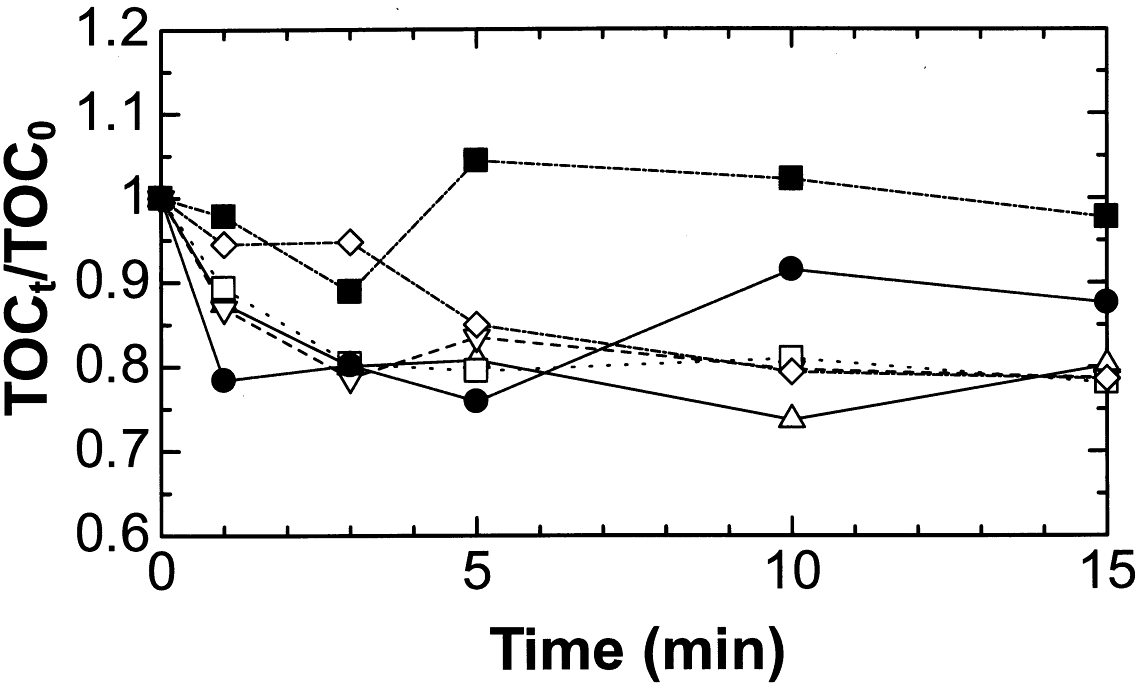

Figure 5-9. Changes in TOC during degradation of Aldrich HA, S1 and S2. [Aldrich HA, S1 and S2] = 30 mg L^{-1}, pH = 7, O_3 = 10 wt%, flow rate = 1 L/min. Open triangles: 15 mg L^{-1}, Reversed triangles: 30 mg L^{-1}, Open rectangles: 75 mg L^{-1}, Diamonds: 150 mg L^{-1}, Solid circles: Ago Bay, Solid rectangles: Ariake Bay.

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CHAPTER 6 GENERAL CONCLUSION

SUMMARY

This thesis was designated in order to make clear the ecological impacts through the environmental monitoring of the artificial tidal flat constructed using solidified sea bottom sediments. The main results of this thesis are as follows; At first, in-situ dewatering and solidifying technique was developed for treatment the contaminated sea bottom sediments (the Hi-Biah-System (HBS)). The products then used to construct the artificial tidal flat in Ago Bay. The ecosystem and environmental conditions of the constructed tidal flats were monitored and compared to the natural ones over the course of 2 years. It was found to be very similar to those of the adjacent natural tidal flat if not better. In the fourth chapter, the use of sea sediments as a substitute for fine sand aggregate was investigated for the fabrication of concrete solids and marine reefs. The composition of the raw materials was optimized, and the different concrete materials were assessed. After 187 days of curing, the compressive strength was 44 MPa for the concrete products with w/c = 0.47 using the sediments. Furthermore, after immersing in the sea environment during approximately one year, the compressive strengths were 48, 33 and 14 MPa for the concretes with w/c = 0.47, 0.69 and 1.15, respectively. These results indicated that the concrete blocks with the sea bottom sediments which were continuously field-tested in the real sea environment for 1 year did not receive any damage from the sea. At the fifth chapter, degradation of humic acids extracted from seabed sediment collected from two different locations was carried out using an ozone treatment technique. Ozonation was demonstrated to be a very efficient technique, and was able to produce a clear color in samples contaminated with marine humic acid within approximately 15 minutes. High molecular weight substances were degraded into low molecular weight substances; however, complete removal was impossible. Degradation of humic acids could be helpful in the restoration of the marine ecosystem in seabed sediments. Moreover, this technique could be used to treat other high molecular weight substances from different wastes.

Recently, large efforts to restore the environmental conditions such as construction of tidal flats, sea grass and sea weed beds have been demonstrated and these mitigation techniques are respected to be able to play an important role in preventing habitat deterioration and in promoting fish nursery grounds in the inner-bay environment. However, there are many problems to develop the applications for environmental restoration. Evaluating the performance of a constructed tidal flat and its environmental and ecological impact is necessary and important for longer time.

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