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Experimental Design in Laboratory for Ecological Restoration in the Slag Dumping Area

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Abstract

Experimental design for ecological restoration approach was investigated from the P' company's slag dumping area with higher pH value. The degree of pH recovery was measured by the injection of carbon dioxide from the LNG exhaust gas, and the residual carbon, for example, calcium and carbonate which can be controlled by artificial seaweed beds. The degree of adaptability from 3 algaes (*Undaria pinnatifida, Sargassum horneri* and *Ecklonia stolonifera*) and uptake nutrient function of *Ecklonia stolonifera* chosen in the first treatment were measured in the laboratory to determine the transplanting algae in artificial seaweed beds. The higher value of pH was decreased to 7.0~8.5 by injection of LNG exhaust gas with flow rate 20 m^3/min. In the experiment design at laboratory, the upper part of frond of *Undaria pinnatifida* and *Sargassum horneri* began to decay, and the color changed after 10 days. However, those of *Ecklonia stolonifera* were after 14~20 days. The uptake rate of nutrient from *Ecklonia stolonifera* was higher than those of other algaes, and those was similar pattern in the control (e.g. seawater); The DIN concentration uptake of *Ecklonia stolonifera* was 1.88 μg/L/hr avg. in leachate, but 2.19 μg/L/hr avg. in seawater. However, the PO_4^{3}-P concentration uptake was 0.18 μg/L/hr avg. in leachate, but 0.31 μg/L/hr avg. in seawater. These result indicated *Ecklonia stolonifera* uptaked these nutrients in the leachate as well as in seawater, and it may suggested for this species to transplant for constructing artificial seaweed beds.

Key Words : Experimental design, Ecological restoration, Slag dumping area, pH value, *Ecklonia stolonifera,* Artificial seaweed beds

1. Introduction

The steel industry was based on the development of shipbuilding, electronic, and automotive fields in advanced country such as Korea. However, this industry had spilled some by-product, e.g. slag, into the neighboring water with increasing pollutants so far[1)]. Higher pH value was in seawater, and the buffering effect was higher in distilled water with the increasing amount of slag[2,3)]. In case of P's company, the total amount of by-product was 2,000 million tons, and then 98.7 % of which was changed to resources for humans[1)]. The remainder was solidified for seawater landfill[1)]. In the previous years, the seawater landfill was 1,400 tons from 1987 to 1995, and will be some tons in 524 thousands m^2 ('97~2010), and 705 thousands m^2 (2011~) every year. The leachate was closed with bank in close to slag dumping area except in the end 100 m of spillways. The pH was 9.5~10.5 in the leachate, and this water diffused through water current in the spillways. Therefore acid was injected for pH recovery, and then predicted some problems for phytoplankton, zooplankton, and other marine organisms.

Recent studies was concentrated on the construction of artificial seaweed beds for improvement of marine

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ecosystems, and increase fisheries resources in Korea[4,5]. However, no reports had been done about an approach of ecological restoration in slag dumping area. This is because the slag dumping area had never been known for people, and it have been difficult for them to control higher pH value among lethal factors for any organisms. On the other hand, the restoration program for mud flat and salt marsh had been reported worldwide[6~8].

The aim of this study was to investigate experimental design in laboratory for ecological restoration in the slag dumping area. Specifically, the objectives are (1) to examine degree of pH recovery, (2) uptake rate of nutrients from 3 algaes (*Undaria pinnatifida, Sargassum horneri* and *Ecklonia stolonifera*) which were measured in the laboratory, and (3) to determine the transplanting algae in artificial seaweed beds. It is a fundamental part of a wider study aimed at understanding the pH neutralization of slag dumping area as well as suitable marine organisms by using carbon dioxide from LNG combustion process, and monitoring the succession of benthic communities after transplanting algae in artificial seaweed beds. It is also first approach for ecological restoration on carbon dioxide reduction in the slag dumping area.

2. Materials and Methods

2.1. The characteristics of leachate and pH recovery

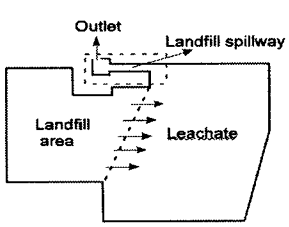
Characteristic of leachate, temperature, salinity, pH, and dissolved oxygen were monitored on each sampling occasion with YSI 6600 instrument. Inorganic nutrient concentrations (NO_3^--N, NO_2^--N, NH_4^+-N, and PO_4^{3-}-P) and chemical oxygen demand(COD) were taken in the study area were measured in the laboratory following the Standard Methods for the Examination of Water and Wastewater Manual[9,10].

The degree of pH recovery in the was measured by the injection of carbon dioxide from the LNG exhaust gas. The location was in the spillways which is only connected with the outside (Fig. 1-a). The LNG exhaust gas systems was composed of constant pressure, and distribution facilities for suitable gas amount. The entrance of them was also consisted of ten 20A pipe with hole, and located in the middle of spillways. The pH sensors was in P1, P2, P3, and P4 and controlled the fluctuation of pH with continuous monitoring (Fig. 1-b).

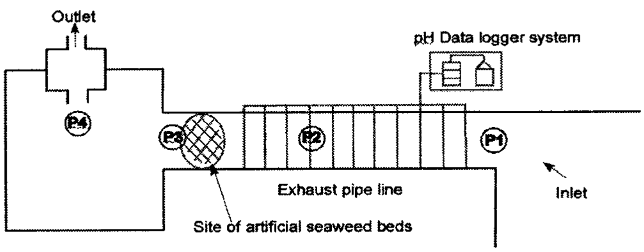
2.2. Experimental design of 3 algaes in laboratory

The three algaes, for example, *Undaria pinnatifida, Sargassum horneri,* and *Ecklonia stolonifera,* were tested with two treatment after the pH value decreased to about 8.0 (neutral value). In the first treatment, three individuals of whole algae (including stipe, blade and holdfast) in three algal species were placed in the 25 L leachate under 12:12 h photo-period. Water temperature of leachate was 11.0℃, pH 9.20, Salinity 28.4, SS 20.5 mg/L, COD 3.2 mg/L, DIN 0.20 mg/L, and PO_4^{3}-P was 0.02 mg/L (Table 1).

In the second treatment, the algal species were placed in the 25 L leachate under 12:12 h photo-period at 15℃ in white fluorescence light condition with con-



(a)



(b)

Fig. 1. The schematic diagram in the study area ; (a) Landfill area (b) Pipe line for injection of LNG exhaust gas and station of pH sensor (P1 : Spillway inlet zone, P2 : Spillway middle zone, P3 : Spillway the last zone, P4 : Outlet zone).

Table 1. Environmental characteristics in the leachate in the first treatment

Temp.(℃)	pH	Sal.(psu)	SS(mg/L)	COD(mg/L)	DIN(mg/L)	PO_4^{3-}-P(mg/L)
11.0	9.20(8.00)	28.4	20.5	3.2	0.20	0.02

trol (seawater) test for estimating of nutrient uptake function after pH value decreased from 9.25 to 8.05. The pH was 8.05 (nearly neutral value), DIN 0.20 mg/L, and PO_4^3-P was 0.02 mg/L in leachate, but pH was 8.10, DIN 0.45 mg/L, and PO_4^3-P was 0.05 mg/L in seawater (Table 2).

3. Results and Discussion

3.1. The characteristics of leachate and pH recovery

The concentration of dissolved oxygen, nitrate, and phosphate was lower, whereas pH (9.25) was higher in the leachate (Table 3). This result was due to inflow the spill water. The CaO in the slag increased pH value with producing OH^- in seawater[11].

$$CaO + H_2O = Ca^{2+} + 2OH^-$$

OH^- was neutralized by CO_2 in LNG exhaust gas, and produced HCO_3^-.

$$CO_2 + OH^- = HCO_3^-$$

The pH value decreased with flow rate of 20 m^3/min by injection of LNG exhaust gas after 12 h in 8 March although it was 8.5~9.0 from 7 March to 8 March (Fig. 2). On the other hand, the pH value was differed with pH sensor location. For example, P1 in close to slag dumping area was the highest, while P4 was lower in the end of spillways. These results were due to difference in the degree of dilution with seawater each locations. The overall pH value was also differed with tide. For example, the seawater flowed into the slag dumping area at high tide, and then pH value was lower and vice versa. Therefore we predicted that constant pH value maintained in the slag dumping area with control time and amount of LNG exhaust gas although injection of LNG exhaust gas was reasonable effect for lower pH value. An automatic LNG exhaust will be needed to maintain constant pH value.

3.2. Experimental design of 3 algaes in laboratory

Undaria pinnatifida was collected from aquaculture farm in Wan Island, Chunranamdo. After 3 days, the color and upper part of frond was changing and water quality of leachate was low with bubbles. Most of *Undaria pinnatifida* began to disappear with increasing time with 80 % loss after 10 days (Fig. 3). *Sargassum horneri* was collected from Dongbak Island, Busan by SCUBA. These species were of similar pattern to those of *Undaria pinnatifida* as time increases (Fig. 4). On the other hand, *Ecklonia stolonifera* was also collected from Bukhyungje Island, Busan with SCUBA. After 2 days, the frond was still in good condition although there was more mucous in the leachate. These similar pattern were remained until 7 days. The stipe and holdfast were better despite the occurrence of a small hole

Table 2. Environmental characteristics in the leachate and seawater in the second treatment

Locations/Items	pH	DIN(mg/L)	PO_4^{3-}-P(mg/L)
Leachate	8.05(9.25)	0.20	0.02
Seawater	8.10	0.45	0.05

Table 3. Environmental characteristics in the leachate of the slag dumping area

Locations /Items	Temp.(℃)	Sal.(psu)	**pH**	DO(mg/L)	TSS(mg/L)	COD(mg/L)	DIN(mg/L)	PO_4^{3-}-P(mg/L)
Leachate	9.8	31.9	**9.25**	7.6	25.3	3.2	0.20	0.02
Seawater	9.8	32.5	**8.18**	8.2	14.3	2.5	0.45	0.05

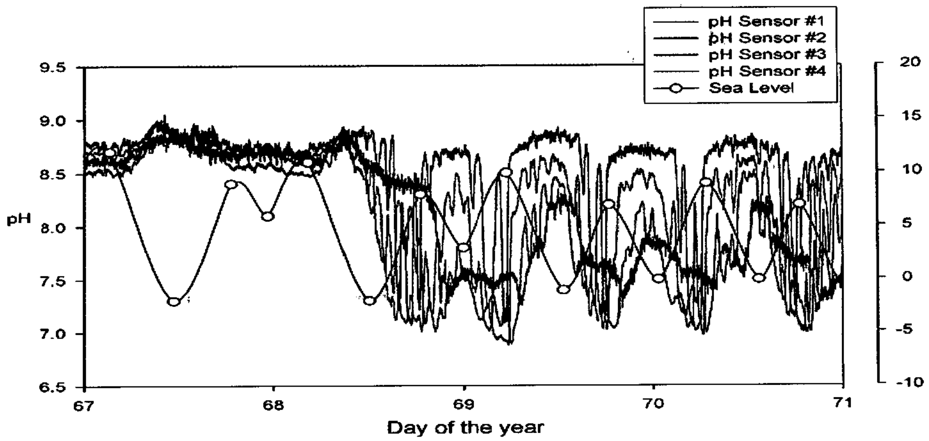
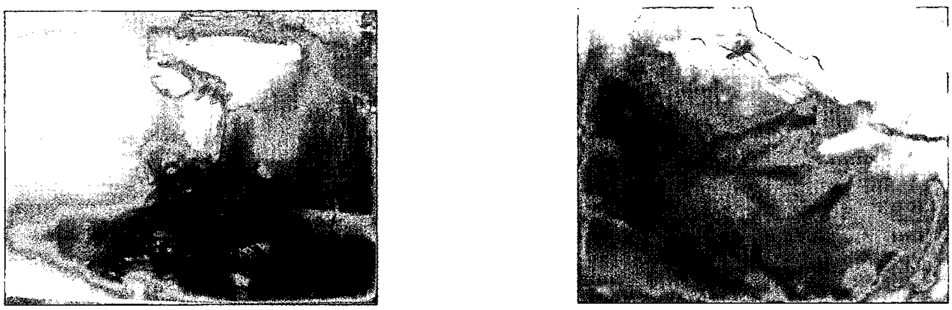
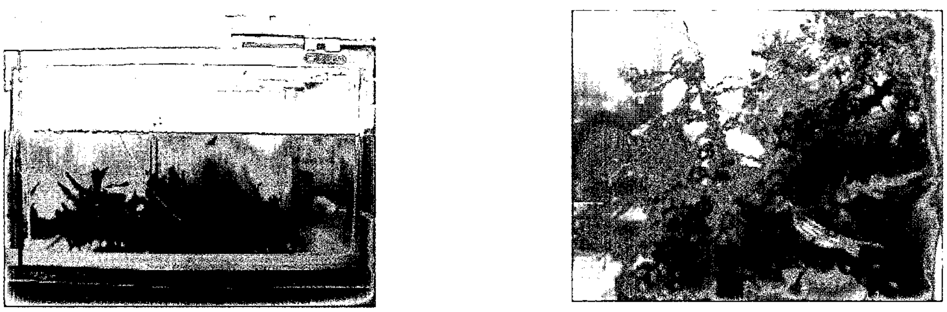


Fig. 2. Temporal variation of pH with injection of 20 m^3/min.



(a) after 5 days (b) after 10 days

Fig. 3. Photography of succession pattern with *Undaria pinnatifida*.

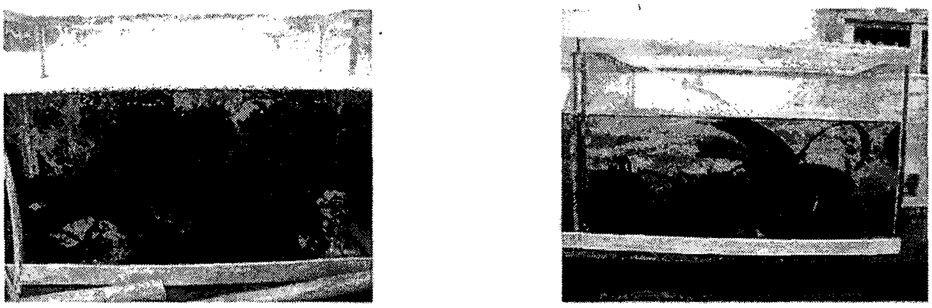


(a) after 5 days (b) after 10 days

Fig. 4. Photography of succession pattern with *Sargassum horneri*.

in each frond compared to other species (Fig. 5).

For the nutrient uptake function of *Ecklonia stolonifera* chosen in experimental design, the DIN, and PO_4^{3}-P concentration in leachate decreased while those in seawater was also decreasing (Fig. 6,7). The DIN concentration uptake of *Ecklonia stolonifera* was 1.88 μg/L/hr avg. in leachate, but 2.19 μg/L/hr avg. in seawater. However, the PO_4^{3}-P concentration uptake



(a) after 10 days (b) after 15 days

Fig. 5. Photography of succession pattern with *Ecklonia stolonifera.*

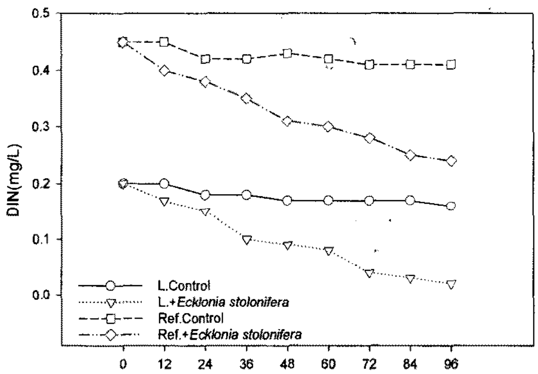


Fig. 6. Temporal variation of DIN in *Ecklonia stolonifera.*

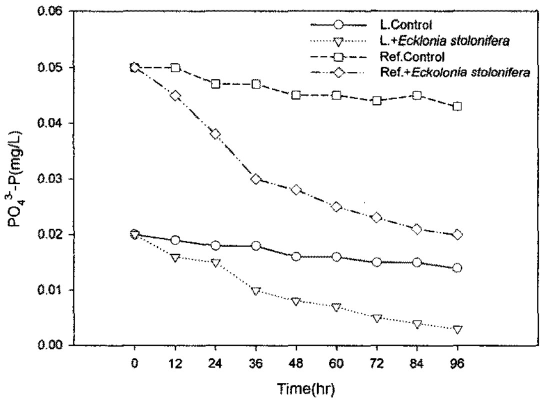


Fig. 7. Temporal variation of PO_4^{3-} in *Ecklonia stolonifera.*

was 0.18 μg/L/hr avg. in leachate, but 0.31 μg/L/hr avg. in seawater. These result indicated that the uptake rate of nutrient in *Ecklonia stolonifera* was similar in patterns for both leachate and seawater. So far, no explanations can be driven from this results. Some studies had already demonstrated that algae has higher photosynthetic capability[12], uptake nutrient[13~15], growth[16], reproductive ability[17], and tolerance to change of environmental characteristics compared with other plants in the seawater. For example, growth rate of *Ulva* was 0.028~0.063 mm/day according to variation of nitrate and phosphate concentration, and then *Ulva* from eelgrass beds is well adapted to oligotrophic water as adjusting its growth and nutrient uptake[18], and biosorption of Pb and Cr by using *Sargassum*[19,20]. Hence we suggested that *Ecklonia stolonifera* uptake these nutrients in the leachate as well as in the seawater, and it may be suggested for this species to transplant at artificial seaweed beds.

4. Conclusions

Preliminary study in laboratory experiment for ecological restoration was investigated from the P' company's slag dumping area. The pH value was in slag dumping area (9.25) than that of in close to seawater (8.18). The higher value of pH was decreased to 7.0~8.5 with flow rate 20 m^3/min by injection of LNG exhaust gas, and this value influenced by location and water sea level. Automatic LNG exhaust gas systems will be provided, if possible, to maintain the constant pH value. In the experiment designed at laboratory, the upper part of frond of *Undaria pinnatifida* and *Sargassum horneri* began to decay, and the color changed with increasing time after 10 days. However, those of *Ecklonia stolonifera* were after 14~20 days.

Thus *Ecklonia stolonifera* have higher adaptability in the leachate. The uptake rate of nutrient by *Ecklonia stolonifera* was higher than those of other algaes. The DIN concentration uptake of *Ecklonia stolonifera* was 1.88 μg/L/hr avg., but the PO_4^{3}-P was 0.18 μg/L/hr avg. in leachate. These result indicated *Ecklonia stolonifera* uptake these nutrients in the leachate as well as seawater, and it may be suggested for this species to transplant for construction artificial seaweed beds. These methods will be useful to control the residual carbon, for example, calcium and carbonate in the slag dumping area. It will be need to monitor the succession of benthic communities on transplanting *Ecklonia stolonifera* for construction artificial seaweed beds based on ecological restoration in the slag dumping area.

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References

1) POSCO, 2007, Creating Another Success Story, Sustainability Report 2007, 102pp.
2) Bajracharya K. and D. A. Barry, 1993, Mixing cell models for non linear equilibrium single species adsorption and transport, J. Contam. Hydrol., 12, 227-243.
3) Chung Y., Y. B. Kim, Y. S. Kwon and S. H. Lee, 1996, Effect of Slag Dumping on Heavy Metals in the Neighbour Sea and Direction of Recycling on Slag, J. Environ. Impact Assess., 5, 21-31.
4) National Fisheries Research & Development Institute, 2007, A study on construction of Seaweed Forest in the East Sea, Aquaculture research division, East Sea Fisheries Research Institute, NFRDI, 198pp.
5) Ministry of Maritime Affairs and Fisheries, 2008, Marine Ranching Manual, MOMAF, 368pp.
6) Odum H. T. and B. Odum, 2003, Concepts and methods of ecological engineering, Ecol. Engin., 20, 339-361.
7) Mitsch W. J., 1988, Ecological engineering and ecotechnology with wetlands: applications of systems approaches. *In* Marani A. (ed.), Advances in Environmental Modelling, Elsevier, Amsterdam, 565-580.
8) Mitsch W. J. and S. E. Jorgensen, 1989a, Introduction to ecological engineering. *In* Mitsch W. J., Jorgensen S. E. (ed.), Ecological Engineering: An Introduction to Ecotechnology, J. Wiley & Sons, Inc., New York. 3-12.
9) Ministry of Maritime Affairs and Fisheries, 2002, Marine Pollution Standard Methods, 330pp.
10) Standard Methods for the Examination of Water and Wastewater, 2005, APHA AWWA WPCF, 10-101pp.
11) Riley J. P. and G. Skirrow, 1975, Chemical Oceanography 2; 2nd edition, Academic press, 647pp.
12) Lapointe B. E., 1987, Phosphorus and nitrogen-limited photosynthesis and growth of *Gracilaria tikvahiae*(Rhodophyceae) in the Florida Keys: an experimental field study, Mar. Biol., 93, 561-568.
13) Fujita R. M., P. A. Wheeler and R. L. Edwards, 1989, Assessment of macroalgal nitrogen limitation in a seasonal upwelling region, Mar. Ecol. Prog. Ser., 53, 293-303.
14) Duke C. S., W. Litaker and J. Ramus, 1989, Effects of temperature, nitrogen supply, and tissue nitrogen on ammonium uptake rates of the chlorophyte seaweeds *Ulva curvata* and *Codium decorticatum*, J. Phyco., 25, 113-120.
15) Littler M. M. and D. S. Littler, 1980, The evolution of thallus form and survival strategies in benthic marine macroalgae: field and laboratory tests of a functional form model, Amer. Nat., 116, 25-44.
16) Chapman A. R. O. and J. S. Craigie, 1977, Seasonal growth in *Laminaria longicruris:* relations with dissolved inorganic nutrients and internal reserves of nitrogen, Mar. Biol., 40, 197-205.
17) Lapointe B. E., M. M. Littler and D. S. Littler, 1997, Macroalgal overgrowth of fringing coral reefs ant Discovery Bay, Jamaica: bottom-up versus top-down control, Proc. 8th Coral Reef Symp., 1, 927-932.
18) Choi T. S. and K. Y. Kim, 2002, Time-dependent variation of growth and nutrient uptake of *Ulva pertusa* Kjellman (Chlorophyta) from intertidal eelgrass beds, Algae, 17, 249-257.
19) Suh K. H., K. H. Ahn, H. S. Lee, H. G. Lee, J. K. Cho and Y. K. Hong, 1999, Biosorption pb and Cr by using *Sargassum sagamianum*, J. Korean Fish. Soc., 32, 399-403.
20) Suh K. H., K. H. Ahn, M. C. Cho, J. K. Cho, H. J. Jin and Y. K. Hong, 2001, *Sargassum confusum* for biosorption pb and Cr, J. Korean Fish. Soc., 32, 1-6.