

Air Pollution Protection onboard by Seawater and Electrolyte

Suk-Heon An[†]

(Manuscript : Received DEC 17, 2005 ; Revised JAN 9, 2006)

Abstract : This research makes a new attempt to apply the activated seawater by electrolysis in the development of two-stage wet scrubber system to control the exhaust gas of large marine diesel engines. First, with using only seawater that is naturally alkaline (pH typically around 8.1), the SO₂ and SO₃ are absorbed by relatively high solubility compared to other components of exhaust pollutants, and PM (Particulate Matter) is removed through direct contact with sprayed seawater droplets. Besides, the electrolyzed alkaline seawater by electrolysis, which contains mainly NaOH together with alkali metal ions (i.e. Na⁺, Mg²⁺, Ca²⁺), is used as the absorption medium of NO_x and CO₂. Especially, to increase NO_x absorption rate into the alkaline seawater, nitric oxide (NO) is adequately oxidized to nitrogen dioxide (NO₂) in the acidic seawater, which means both volume fractions are adjusted to identical proportion. The results found that the strong acidic seawater was a valid oxidizer from NO to NO₂ and the strong alkaline seawater was effective in CO₂ absorption. In the scrubber test, the SO_x reduction of nearly 100% could be achieved and also led to a sufficient PM reduction. Hence, the author believes that applying seawater and its electrolyte would bring the marine air pollution control system to an economical measure. Additionally, it is well known that NO_x and SO_x concentration has a considerable influence on the N₂O emission of green house gas. Although the N₂O concentration exhausted from diesel engines is not as high, the green house gas effect is around 300 times greater than an equivalent volume of CO₂. Therefore, we investigated the N₂O removal efficiency with using the electrolyzed seawater too. Finally, this research would also plan to treat the effluent by applying electro-dialysis and electro-flotation techniques in the future.

Key words : Marine air pollution , Seawater, Electrolyte

1. Introduction

When compared with automotive engines, it is very difficult to control the

exhaust emissions of large marine diesel engines because they have exceedingly large output and use usually the lowest quality fuels. In contrast to the number of

[†] Corresponding Author(Surveyor, GL in Japan) E-mail : shann6801@hotmail.net
TEL & FAX : +81-78-413-3173

post-treatments proposed to reduce NO_x from marine diesel engines, only SCR (selective catalytic reduction) has been viewed as an effective method until now⁽¹⁾⁽²⁾. On the other hand, the wet scrubber system using seawater has been used to control exhaust emissions, particularly for SO_x removal, not only for marine diesel engines but also for land-based industrial and utility applications⁽³⁾⁽⁴⁾. As an example, the SO_x component is condensed by cooling the exhaust gas stream to below the dew point, and the SO_x concentration is reduced about 90% or more, with the pH of the scrubber seawater decreasing from 8.01 to 2.95, i.e. from alkaline to acidic. However, such systems are not yet available commercially to comprehensively control pollution.

Considerably less work has been done on the effect of electrolyzed seawater on the removal efficiency of exhaust gas components and studies to date have only investigated the usage of seawater itself.

This research is undertaken to develop a new method to target elimination of all exhaust emissions, particularly onboard, because the vessel can easily adapted to use seawater for the application of a wet scrubber system when compared with an automotive engine. In a recent report⁽⁵⁾⁽⁶⁾, it was found that the electrolyzed seawater is an interesting possibility since the strong acidic and alkaline seawaters play an important role in NO oxidation and CO₂ absorption respectively. I have pursued this finding in greater detail by examining the dependence of electrolyzed seawater pH. It was reported that the boundary conditions available for the

reduction of exhaust gases were investigated by simultaneous examination of the actual scrubber and the bubbling test with the varying seawater pH.

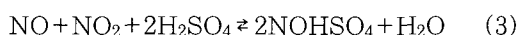
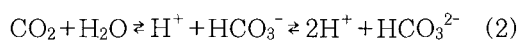
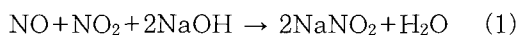
2. New Application of Marine Air Pollution Control

When a slow speed diesel engine operating on heavier fuel oil and at normal service load (around 80% MCR), the actual composition of the exhaust gas stream is typically as follows: PM 120mg/m³, SO₂ 660ppm, NO_x 1220ppm, HC 120ppm, CO 50ppm, CO₂ 5.6%, O₂ 13.6%. The exhaust gas properties from the combustion of heavier fuel oil, which is used generally in marine diesel engine, are shown upon the whole to be strongly acidic, pH 2.5 to pH 3.5⁽⁷⁾.

2.1 Two-stage wet scrubber system

Fig. 1 shows the schematic of our new model (known as the Two-Stage Wet Scrubber System) for marine air pollution control. First, the exhaust gases flow into the 1st-stage via a funnel, and are treated by scrubbing only, with seawater to target SO_x and PM removal. Now, the exhaust gases need to be thoroughly mixed with seawater spray to remove the SO_x by absorption. PM is removed directly into seawater droplets by contact impaction and the removal effect is proportional to impaction numbers between particles and seawater droplets. As a result, the combined reaction is to neutralize various pollutants, wash them out and dilute them. Thereby there would be expected to be a reduction of 93 to 98% of SO_x, 85 to

90% of PM, 20 to 30% of NO_x, and 5 to 10% of CO_x as in CO and CO₂ as shown on the bottom-right of the fig. In the second stage, the electrolyzed alkaline seawater absorbs or adsorbs the remaining NO_x and CO₂ untreated at the first stage. However, in advance, NO is adequately oxidized to NO₂ by using the electrolyzed acidic seawater of pH 3 because NO_x absorption is the most suited to conditions when both volume fractions (NO:NO₂ ratio) are equal portions as shown in equation (1). Equation (2) shows the various relations in terms of pH when carbon dioxide is dissolved in water. Especially, the bicarbonate ions contained in the alkaline seawater have buffering potential against the strong acidity, and it therefore would be capable of adjusting the pH of the effluent.



Furthermore, as the effluent contains a large amount of sulfuric acid in the first stage, it also has sufficient possibility to be capable of absorbing NO in the acidic seawater. In this case, the chemical compounds of violet acid (H₂SO₄·NO) and nitrosylsulfuric acid (NOHSO₄) would be formed and the formula is as the above-mentioned equation (3).

2.2 Seawater electrolysis

Fig. 2 presents the schematic of seawater electrolysis. Seawater is an electrolyte

solution as a weak alkali. Its chemistry is dominated by the presence of six ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻), which constitute more than 99.5% of the dissolved constituents. In an electrolytic bath the ions are separated so that cations and anions move towards positive and negative sides respectively. Na⁺ ions gathered close to the negative pole react with OH⁻ ions produced from H₂O, thereby NaOH aqueous solution is produced at the negative side. It is accompanied by the production of H₂ and Cl₂, however, the chlorine gas evolved may be appropriately controlled by increasing the flow rate of seawater into the electrolytic bath, and the sodium hydroxide forms constituents of strong alkaline seawater. The chief pollutants react with H₂O and O₂ and are absorbed into NaOH aqueous solution. The expected absorption reactions are summarized in Table 1. Both negative and positive electrodes will be made of titanium with platinum, and the diaphragm made of polytetrafluoroethylene.

Table 1 Expected reaction processes

SO ₂	$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$ $\text{H}_2\text{SO}_3 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$ $\text{H}_2\text{SO}_3 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O}$ $\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
NO	$2\text{NO} + \text{O}_2 \rightarrow \text{N}_2\text{O}_4$ $\text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$ $\text{HNO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$ $\text{HNO}_2 + \text{NaOH} \rightarrow \text{NaNO}_2 + \text{H}_2\text{O}$
CO ₂	$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$ $\text{H}_2\text{CO}_3 + \text{NaOH} \rightarrow \text{NaHCO}_3 + \text{H}_2\text{O}$ $\text{NaHCO}_3 + \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$

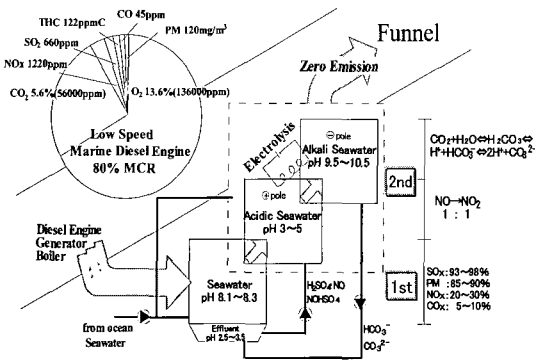


Fig. 1 New model of marine air pollution control

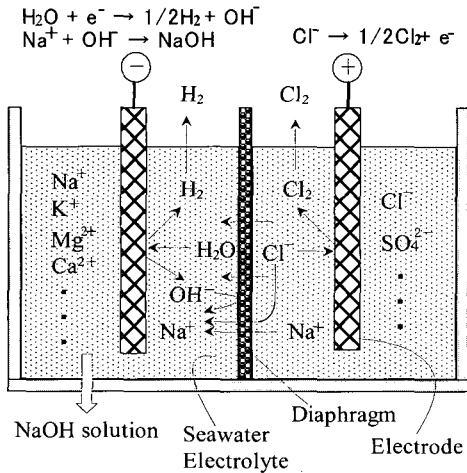


Fig. 2 Seawater electrolysis

3. EXPERIMENTAL METHODS AND EQUIPMENTS

One objective of this experiment was to compare the effects of reaction seawater pH on NO, N₂O and CO₂ control by the standard gas-bubbled test in an electrolytic bath. The other objective was to investigate the reduction effect of various pollutants while actually scrubbing the exhaust gases.

3.1 Bubbling test of standard gases

Fig. 3 displays the experimental appa-

ratus bubbled with NO, N₂O and CO₂ standard gases. Each bath of positive and negative poles was filled with 2dm³ of seawater, and electric current adjusted to produce the desired pH. Then, each standard gas was bubbled in the electrolytic baths, and each concentration was measured at the inlet and outlet. The effects of reaction water pH and temperature, the changes of pH after the bubbling, the relation between the quantity of reaction water and gas components were investigated.

3.2 Scrubber test of actual exhaust gases

Fig. 4 depicts the schematic of the scrubber test undertaken with the actual exhaust gases from a large-scale combustor using a heavy fuel oil as shown in Table 2. The combustor is around 60kW as the fuel consumption is around 11~13kg/hr.

The exhaust gas amount was from 3.6 to 5.6m³/min as with the air excess ratio from 1.96 to 1.25. The exhaust gas from the combustor with heavy fuel oil is conducted through the exhaust pipe into the scrubber. The scrubbing seawater washes out the exhaust gas by injecting the seawater through spray nozzles in a once-through operation. The cleaned gas, therefore, was discharged into the atmosphere after scrubbing. The total reaction seawater (0.02 m³/min) injected though 3 nozzles was fed at only 0.3 % against the exhaust gas amount. To take account of the buoyancy of exhaust gas, the reaction seawater from the first nozzle was configured to form a thin liquid layer constantly moving toward the

exhaust stream and the others were sprayed and atomized to counter-flow it. A porous pipe layer was also established on the inside of scrubber to ensure that exhaust gas and water reacted easily. Finally, SO₂ and PM (Dry Soot (DS), Soluble Organic Fraction (SOF)) concentrations and the exhaust gas temperature were measured at the inlet and outlet of scrubber. Generally, about 10 minutes were required for each sample to reach a stable measurement. As shown in Table 3, the properties of reaction seawater were, respectively, pH3.3 acidic and pH9.3 alkaline by electrolysis, pH7.9 mixture of the two was pH7.9 and pure seawater was pH8.0.

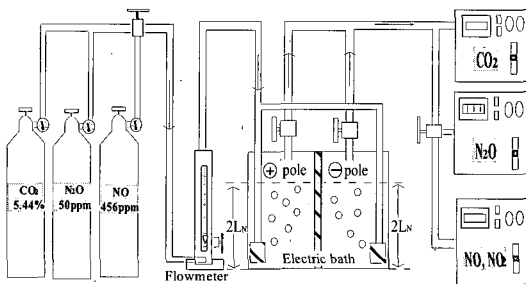


Fig. 3 Experimental equipment of bubbling test

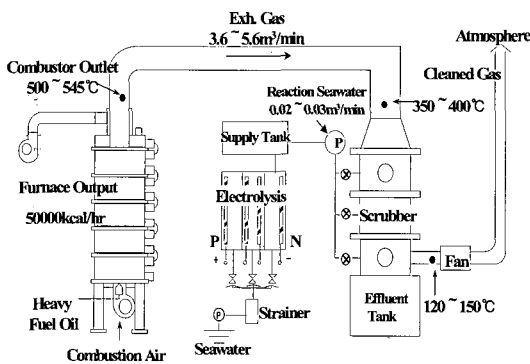


Fig. 4 Schematic of scrubber test

Table 2 Fuel oil property

Density	0.982 g/cm ³
Flash point	74.0°C
Kinematic viscosity(50°C)	177.0 cSt
Pour point	-10.0°C
Residual carbon	12.3 mass%
S	2.56 mass%
H ₂ O	0.50 mass%
Ash content	0.02 mass%
High calorific value	42.78 MJ/kg

Table 3 Experimental condition of scrubber test

Scrubber		Inlet	Outlet
Temp. (°C)	Exh. gas	430	130
	Reaction seawater	31	41
pH of reaction seawater		3.3	2.7
		7.9	3.4
		8.0	2.8
		9.3	3.1

4. EXPERIMENTAL RESULTS AND DISCUSSIONS

It is the purpose of this paper to introduce the usage of seawater and its electrolysis for the exhaust emission control in marine diesel engine. However, scrubbing flue gases with seawater are a proven industrial desulfurization process, and the technique using water to treat the particulate matter has been used for a long time. Accordingly, the bubbling test was mainly carried out to qualitatively grasp the effect of electrolyzed seawater pH on the removal possibility using NO, N₂O and CO₂, and the scrubber test was the main target of SO_x and PM removal effect.

4.1 bubbling test

First, Fig. 5 illustrates an example of seawater electrolysis producing pH10 and pH3 at the respective poles. Generally, it is known that the theoretical cell voltage is around 2.2V and around 0.67kAh is required to produce 1 kiloliter of purified NaOH by electrolyzing the salt-solution. When using D.C. 3V/2A in this experiment, it took about 10 minutes (around 36Wh) to obtain each 2dm³ of alkaline and acidic seawater at 15°C.

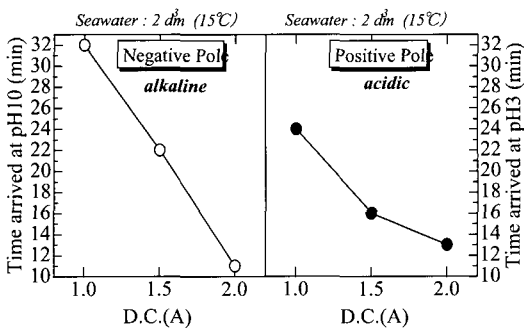


Fig. 5 Seawater electrolysis test

Fig. 6 shows NO oxidation rate changed by reaction seawater pH. The oxidation increased suddenly in strong acids of less than pH5, but there was no significant variation in reaction over pH6 of weak acid to strong alkaline. This was confirmed when the graph is divided into two parts-acidic and alkaline: NO concentration was lower and NO₂ is higher in the acidic area, thereby NO is high and NO₂ is almost zero in the alkaline. The reaction seawater pH between before and after of the bubbling does not change significantly and it is shown by the straight diagonal line.

Fig. 7 shows N₂O removal efficiency

changed by reaction seawater pH when using 50ppm standard gas. N₂O concentration was reduced from around 50ppm to 35ppm on an average and the removal efficiency increased slightly in the acidic area. The pH after bubbling was slightly increased.

Fig. 8 displays CO₂ removal efficiency changed by reaction seawater pH. With an increase of the reaction seawater pH, CO₂ concentration decreased and, especially, the removal effect was high at pH10, strong alkaline seawater. In discussing major specific chemical species in alkaline seawater, we will consider first the constituents that consist of, and combined with, H₂O (and OH⁻), NaOH and the cations Na⁺, K⁺, Ca²⁺, Mg²⁺ etc. The proportions of CO₂ absorption showed respectively 63%, 44.7% and 17.7% when the reaction seawater pH changed to pH10, pH9 and pH3. It will be necessary to use strong alkaline seawater, higher than pH9.5 in order to remove 50% or over there was little change to reaction water pH between before and after the bubbling.

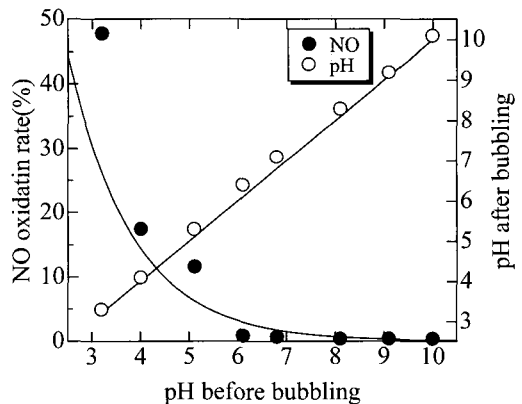


Fig 6 NO Oxidation rate changed by pH

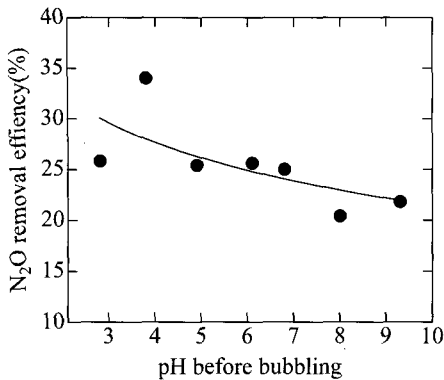


Fig. 7 N₂O Removal efficiency changed by pH

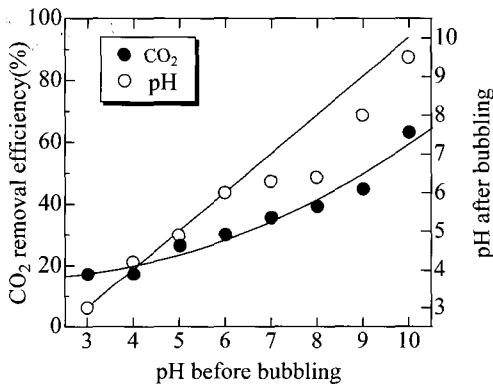


Fig. 8 CO₂ Removal efficiency changed by pH

4.2 Scrubber test

In the results from of scrubbed exhaust emission, the SO₂ was nearly 100% removed in any reaction water pH, as shown in Fig. 9, due to the high solubility of SO₂ in seawater. Meanwhile, the application of seawater to control off gas sulfur can be considered an appropriate method because seawater typically contains some 2000ppm magnesium sulfate(MgSO₄) and 1200ppm calcium sulfate(CaSO₄) respectively around 6% and 4% of the total dissolved solids some 10¹⁵ tones of sulfur as sulfate overall. Accordingly, it is considered that utilization of only seawater would be suitable for absorption of SO₂. It has generally been expressed that the

hydrocarbon and particulate matters could have a detrimental environmental effect. Fig. 10 displays the reduction of SOF and DS by scrubber. In any case, SOF was removed nearly perfectly and DS was washed out at about 50%. The SOF removal effect was rather higher than DS in the entire particulate matters. It is assumed that most of the SOF compounds play a significant role in the formation of soot aggregates and therefore the large SOF-containing particles are apt to be contacted with sprayed water droplets.

Photo 1 depicts the particulate matter sampling from the effluent tank after scrubbing the exhaust gases. It was found that light and small particles mainly existed at the surface of effluent tank, and their aggregations were observed at the bottom. Therefore, this research would plan to treat the effluent by applying electro-dialysis and electro-flotation techniques in the future.

Finally, Table 4 illustrates the properties of the seawater before electrolysis, the electrolyzed acidic and alkaline seawaters, and the effluent after scrubbing. Especially, we notice that the specific electric conductivity and the calcium hardness were increased in the effluent after scrubbing.

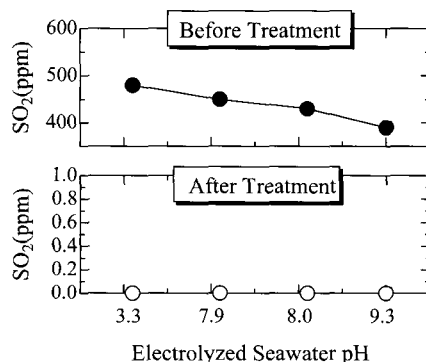
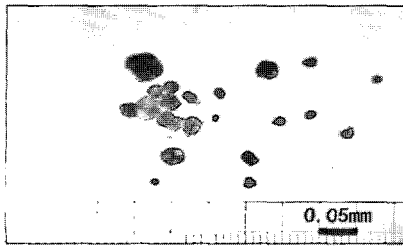
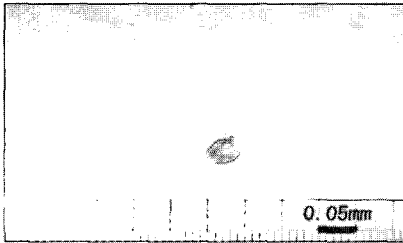


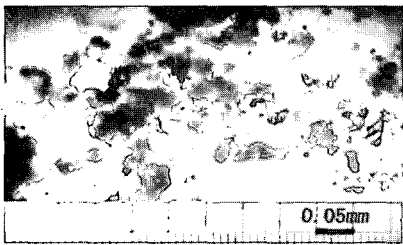
Fig. 9 SO₂ Removal changed by pH



(a) Surface of Effluent Tank



(b) Middle of Effluent Tank



(c) Bottom of Effluent Tank

Photo 1 PM of effluent tank after scrubbing

Table 4 Reaction Water Properties

	Seawater Before Electrolysis	Acidic	Alkaline	Effluent After Scrubber
pH (25°C)	8.09	2.00	9.84	2.76
Specific Electric Conductivity (mS/m) (25°C)	3900	4170	3800	4790
M Alkalinity (pH4.8) (mg CaCO ₃ /L)	60	0	60	0
Total Hardness (mg CaCO ₃ /L)	3640	4360	3120	5600
Calcium Hardness (mg CaCO ₃ /L)	640	720	700	1000
Cl ⁻ (mg Cl ⁻ /L)	12000	12000	12000	108
SO ₄ ²⁻ (mg SO ₄ ²⁻ /L)	1480	2180	2040	3040
Fe (mg Fe /L)	0	0	0	1.32
SiO ₂ (mg SiO ₂ /L)	0.5	0.1	0	4.0
T-PO ₄ ³⁻ (mg PO ₄ ³⁻ /L)	0	0	0	0
Cu ²⁺ (mg Cu ²⁺ /L)	0	0	0	0
NH ₄ ⁺ (mg NH ₄ ⁺ /L)	0	0	0	0
S ²⁻ (mg S ²⁻ /L)	0	0	0	0
Total Evaporation Residuum (mg/L)	30420	32526	29640	30565

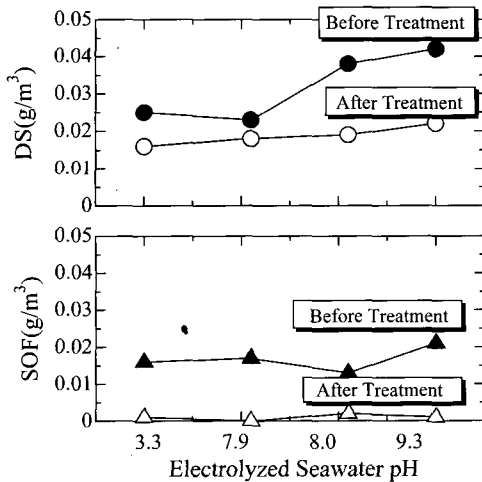


Fig. 10 PM removal changed by pH

5. CONCLUSION

In the bubbling experiment, the results showed that the NO was oxidized to NO₂ at pH3, strong acidic seawater, and the removal of CO₂ was effective at pH10, the strong alkaline seawater; there was little change in pH on the absorption of N₂O. This suggests that seawater electrolysis is suitable for absorption of NO_x and CO₂.

In the scrubber experiment, the SO_x removal could be achieved nearly perfectly and also led to a sufficient reduction of PM without regard to the pH values of reaction seawater. It is supposed that the

scrubber has the sufficient ability to control SO_x and PM even though using only seawater. However, it may be also necessary to do a trial for NO_x and CO₂ absorption using the electrolyzed seawater.

Advantages of the seawater scrubber system include the fact that operation using heavy fuel oil would be possible, retaining a simple treatment system without the need to change over fuel oil grades prior to SO_x exhaust emission control areas and other areas where low sulfur emission rates are required.

REFERENCE

- [1] P. Christoffersen, "Progress in SCR DENOX and Silencing Technology for Diesel Engine Exhaust Systems", 22nd CIMAC Congress, Copenhagen, (1998).
- [2] A.A Wright, B.L. Burlingham, "The SCR Option", Institute of Marine Engineers, Paper 14 IMAS 96, (1996).
- [3] Marine Engineers Review, "Can a SO_x Scrubber be an Economic Alternative to Low Sulphur Fuel", Institute of Marine Engineers, London, (June, 1995).
- [4] Nyman, Goran B.G. and Tokerud Arvid, "Seawater scrubbing removes SO₂", Oil & Gas Journal, (Vol.89-No.26, 1991), pp.52-54.
- [5] O. Nishida, S. An, H. Fujita, W. Harano, D. Lee and M. Tashiro, "Development of Flue Gas Desulfurization System by Applying of Seawater Electrolysis", Proceedings of The Third Asia-Pacific Conference on Combustion in Korea (2001), pp. 377-380.
- [6] S. An, O. Nishida, H. Fujita, W. Harano, M. Hiroi, M. Sato, M. Tashiro and H. Kim, "Basic Research for Using Electrolyzed Seawater in Air Pollution Control System Development of Large Marine Diesel Engine", Proceedings of Busan International Symposium 2001 in Korea (2001), pp.267-271.
- [7] S. An, O.Nishida, H. Fujita, W. Harano, D. Lee, "Characteristics of Combustion and Emission on the Low Grade Heavy Fuel Oil", TECHO-OCEAN2000 International Symposium in Japan, (Vol. 3, Nov. 2000), pp. 765-768.

Author Profile



Suk-Heon An

1992년 2월 한국해양대학 기관학과 졸업, 1998년 8월 한국해양대학 기관학과 동력기계 전공 석사, 2002년 9월 고베대학(구 고베상선대), 2002년 10월 - 2004년 11월 해양기계에너지 전공, 미국선급(ABS), 2004년 12월 - 현재 독일선급(GL)