

Development of Marine Emission Control System on NO_x and SO_x through Seawater Electrolysis

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Abstract : In marine air pollution control, SCR (Selective Catalytic Reduction) is reconized as the most effect method to control NO_x, but on the other hand, seawater scrubber applying the basic characteristic that is naturally alkaline (pH typically around 8.1) is viewed as an economical SO_x removal system at present.

Especially, seawater scrubber would not be necessary to follow any of the various land based flue gas desulfurization methods, i.e. wet, dry or alkali scrubbing. However, these methods are not readily adaptable to marine conditions due to the quantities of consumables required, i.e. lime or limestone, the means of operation and the commercial availability.

This research is undertaken to develop a new method as the main target of eliminating all exhaust emissions, particularly vessel, because of easy access to seawater and apt to apply a wet scrubber system. First, using the acidic seawater by seawater electrolysis, nitric monoxide(NO) is adequately oxidized to nitric dioxide (NO₂) by ClO_x⁻ in the acidic seawater, the electrolyzed alkaline seawater by electrolysis, which contains mainly NaOH together with alkali metal ions (i.e. Na⁺, K⁺, Mg²⁺, Ca²⁺), is used as the absorption medium of NO_x, the SO_x are absorbed by relatively high solubility compared to other components of exhaust pollutants. The results found that the NO_x and SO_x removals could be achieved nearly perfect.

Key words : Marine pollution control, Wet Scrubber, Seawater, Electrolysis, ClO_x⁻ ion

1. Introduction

For reducing atmospheric contamination materials such as nitric oxide compound and sulfur oxide discharged from a vessel, IMO's discussion on a regulation of discharge fixed an outline by adopting a

protocol for new addition [Regulations on Prevention of Atmospheric Contamination by Vessels] and the ANNEX VI to MARPOL 73/83 during the Conference of the Countries of Convention on the Prevention of Marine Pollution held in September, 1997.

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Considering the rate of using the contamination materials on shore, a measure for reducing NO_x, SO_x, and PM discharged from vessels sailing within the coastal area of 200 nautical miles is urgently required. The vessels coming under the regulations of IMO are those of 130kW/400 tons or larger, the sulfur ingredient of fuel to be used should be 1.5wt% or 6g/kWh or less for the restriction of SO_x, and NO_x should be $45 \times n^{-0.2}$ g/hWh or less ($n = \text{rpm}$, $130 < n < 2000 \text{rpm}$)

Also, as the sizes of the vessels are 2000~3000tons or less, the equipment for treating the exhaust gas should be small, light, and highly-efficient. Accordingly, this study will discuss on reducing NO_x for vessels by electrically decomposing seawater.

It is reported that the atmospheric contamination materials(Nitric Oxide and Sulfur Oxide) discharged from vessels amount to 4~7% of those of the whole globe. The generation of SO_x is little influenced by the combustion status and is dominated by the sulfur ingredient of fuel. Most of the fuel sulfur(S ingredient) becomes SO₂ and the rest of it SO₃ by cooling. SO₂ greatly influences the human body and a small dose is very fatal. SO₃ generates a snow smut by sticking to a particle or lactic acid by reacting with vapor. Furthermore, it becomes a cause for nose breath due to low temperature. A combination of SO₂ and SO₃ is defined as SO_x. When the fuel of 50 thousand cases from real vessels were sample-tested, the average density of sulfur ingredient was 2.9 mass%. The quantity of SO_x discharged from vessels, estimated from a summary of energy related to

vehicle-operation of 1999 (compiled from the information control department of the bureau of vehicle related policy in japan) was 985,000 tons and its nearly 95% was generated from C heavy oil.

With the economic loss being reduced, the scrubber method using the seawater or the water made by the electrolysis treatment of the seawater was proposed and its basic experiments were carried out.

2. Experimental (Chlorine Gas)

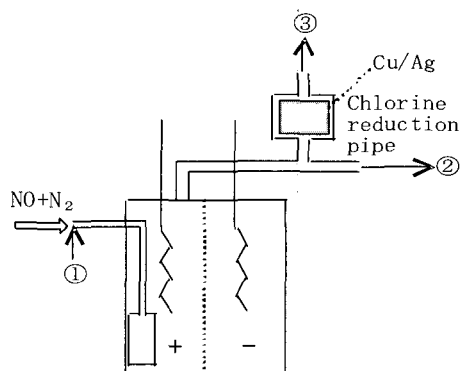


Fig. 1 Schematic diagram of Electrolyzer

Cl₂ generated from the plus terminal by electrically decomposing seawater will age the function of a detector due to NO_x measurement instrument and decrease its life. A metallic filter for reducing chlorine gas by absorbing it into the upper field of the measurement instrument were discussed. The equipment and filter was shown on Fig. 1.

Silver(25~35meshes) and copper granules (0.2~0.9mm) were used to reduce Cl₂ gas. The speed of a current of the supplied gas which was 0.3 ℓ/min was regularly measured against the electrolysis time. The result is shown on Table 1 and 2.

Table 1 Result of silver side

Time (min)	Measure point ②			Measure point ③		
	NO ₂ (ppm)	NO(ppm)	Cl ₂ (%)	NO ₂ (ppm)	NO(ppm)	Cl ₂ (ppm)
0	0	200	0	0	200	0
2	※	※	3	※2.5	0	0
5	※	※	4	※	※	200

(Ag) : 25-35 meshes

Current NO+N₂ : about 0.3 l/min

(※) unknown

Table 2 Result of copper side

(min)	Measure point ②			Measure point ③		
	NO ₂ (ppm)	NO(ppm)	Cl ₂ (%)	NO ₂ (ppm)	NO(ppm)	Cl ₂ (ppm)
0	※	※	2.2	0	120	0
2	※	※	3.2	0	80	0
5	※	※	4.0	※	140	100

(Cu) : 0.2-0.9mm

Current NO+N₂ : about 0.3 l/min

(※) unknown

3. Experimental (NO_x Gas)

3.1 The result of the basic experiment for reducing NO_x

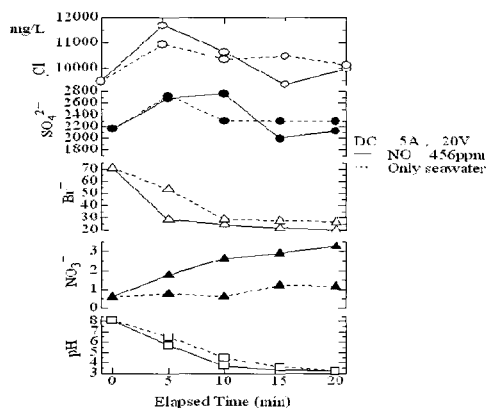
**Fig. 2 The changing density of ions against the electrolysis time**

Fig. 2 shows the changing density of ions against the electrolysis time. The solid line is the result which appears

when NO gas(initial density 456ppm) is supplied by 5ℓ/min. The dotted line is the result which appears when NO gas is not supplied. Although it appears that, as the electrolysis time is longer, the density of various ions including pH tends to be lower when NO gas is supplied than when it is not supplied, NO₃ ions considerably increased. This is because nitric acid is generated when NO was dissolved into water.

3.2 NO Reduction Experiment by a Small Two-Towered Scrubber

It will be examined how it is efficient when NO gas of initial density of 160ppm is flowed in by 3ℓ/min, with each 0.5ℓ/min of alkaline(pH 9.8) and acid(pH 2.6) water treated in a II-type table electrolyzer being supplied into a small scrubber(Fig. 3).

The effects by the electrolysis water against the lapsing time was shown Fig. 5. Slanted obstruction plate(6 plates) and a fiber mat were installed in the scrubber for the efficiency of response. As shown in the figure, NO was reduced by about 90% and NO₂ completely.

(1) In case being scribed by the electrolysis seawater, NO was reduced by about 90%.

(2) NO was not reduced by only seawater.

(NaSO₄) solution was used for the electrolysis solution of seawater. The chlorine ions influence on the solution response of NO was examined. A small two-towered scrubber of Fig. 4 was used in the experiment. Each 0.5ℓ/min of anode and cathode solution with pH of 2.9 and 9.8 were supplied.

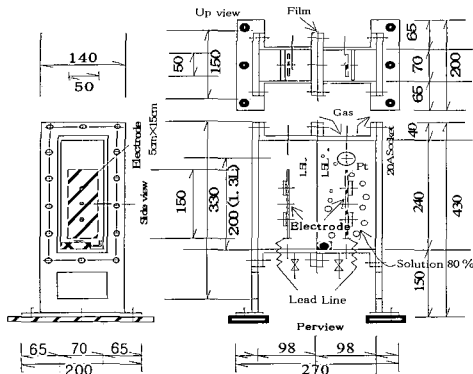


Fig. 3 Π -type table electrolyzer being supplied into a small scrubber

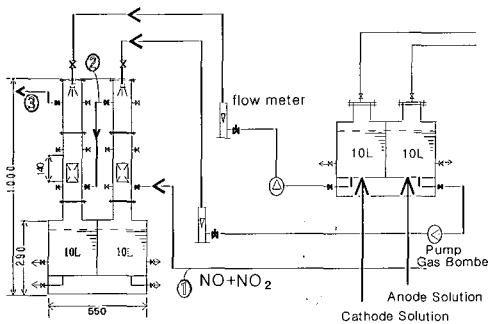


Fig. 4 A small two-towered scrubber

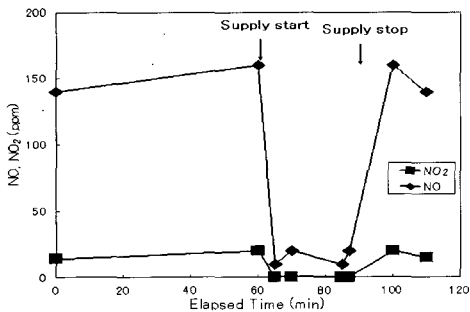


Fig. 5 The effects by the electrolysis water against the lapsing time

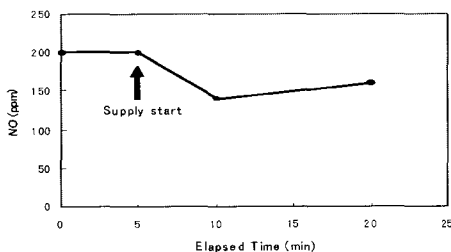


Fig. 6 The result measured against elapsed time at the exit ③ of the scrubber

The result measured against lapsing time at the exit ③ of the scrubber, with gas with the initial density 200ppm of NO being flowed in by 3 ℓ /min, was shown on Fig. 6. As shown on the figure, although NO is lowered after 10 minutes, there is a little effect on NO reduction. It can be assumed also that, even with high acid solution concentration, the oxygen ion is not effective, and that the role of the chlorine ion compound is of more importance.

4. Experimental (SO_x Gas)

4.1 The Effect of Reducing SO₂ and Changing Density of Ions by the Alkaline Water(I-type table electrolyzer used)

For the experiment using both only seawater and the alkaline water, the density of SO₂ was measured at the exit after letting 1 ℓ /min of the SO₂ standard gas(785ppm) flow in each 100ml of both waters. The solutions were analyzed also with a chromatograph.

Table 3 SO₂ density and pH against the flow time of SO₂ for the seawater

min	pH	°C	SO ₂ (ppm)
0	7.7	23.6	700
5	5	23.2	0
10	3	22.6	0
15	2.7	22.7	80
20	2.6	23.6	233

SO₂(785ppm)current 1L_N/min Seawater pH7.7 temperature 23.6°C

Volume of seawater : 100ml

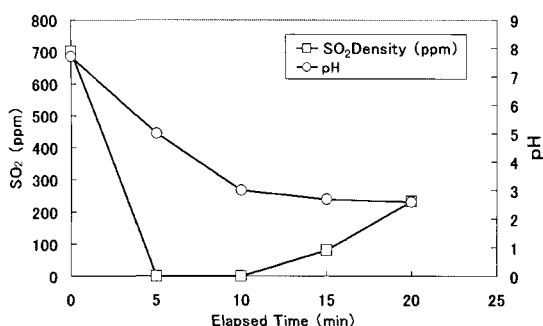


Fig. 7 SO₂ and pH against the flow time of SO₂ for the seawater

Table 3, Fig. 7, Table 4 and Fig. 8 show the variation of the SO₂ density and pH against the flow time of SO₂ for the seawater and the alkaline water each. For the seawater, SO₂ was completely reduced until its flow time reached 10 minutes and ppm was increased at the exit due to the saturation of seawater after the flow time passed 15 minutes or more. For the alkaline water, SO₂ was completely reduced until its flow time reached 20 minutes and ppm was increased at the exit due to the saturation of alkaline water after the flow time passed 25 minutes or more. Both for the seawater and the alkaline water, pH was decreased after SO₂ was flowed through, was 2.6 for the seawater (when the flow time is 20 minutes) and 2.7 for the alkaline water (when the flow time is 25 minutes). Fig. 9 and 10, with an ion chromatograph, show how the density of SO₃²⁻ and SO₄²⁻ changed both in the seawater and in the alkaline water after SO₂ flowed through. Although the density of SO₃²⁻ ion was increased in both waters as the flow time was increased, the increase was significant for the seawater and little for the alkaline water.

The density of SO₄²⁻ was fixed as it was not oxidized.

4.2 The Effect of Reducing SO₂ with a Two-Towered Scrubber (a II-type table electrolyzer used)

Table 4 SO₂ density and pH against the flow time of SO₂ for the alkaline water.

min	pH	°C	SO ₂ (ppm)
0	10	25	700
5	9	24.2	0
10	6.3	23.8	0
15	3.4	23.2	0
20	2.8	23	0
25	2.7	23	211

SO₂(785ppm) current 1L/min Seawater pH7.8
Temperature : 25.0°C

Alkaline water pH 10.0 Temperature : 25.0°C
Volume of Alkaline water : 100ml

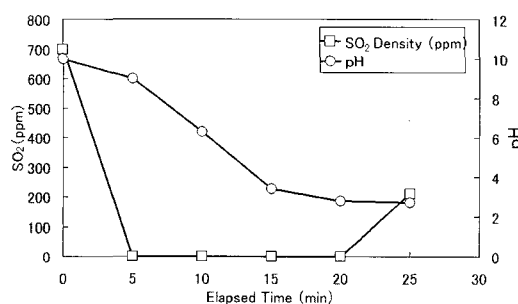


Fig. 8 SO₂ and pH against the flow time of SO₂ for the alkaline water

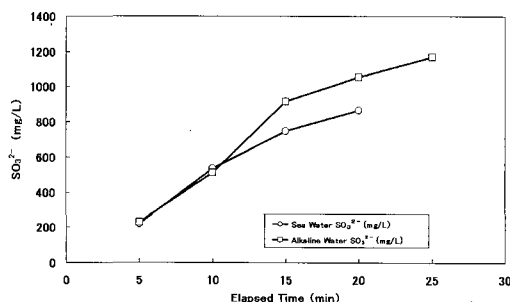


Fig. 9 Change of SO₃²⁻ density

The results of supplying 2 litters/min of SO_2 gas(700ml) after letting 0.5 litters/min of the seawater flow on each of both sides were shown on Fig. 11.

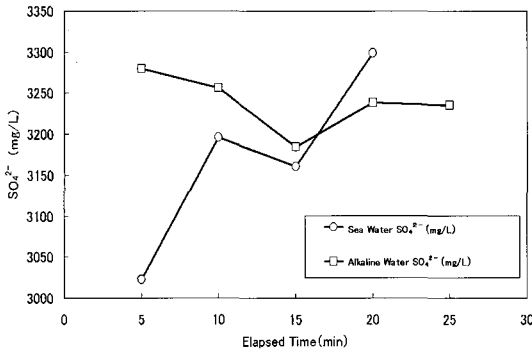


Fig. 10 Change of SO_4^{2-} density

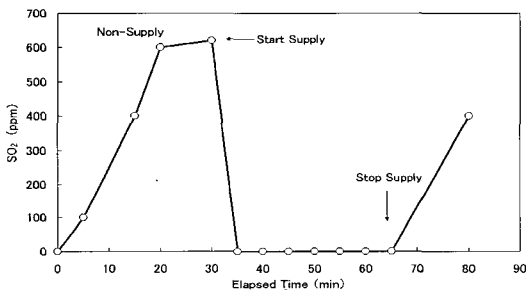


Fig. 11 The Effect of Reducing SO_2 with a Two-Towered Scrubber (seawater)

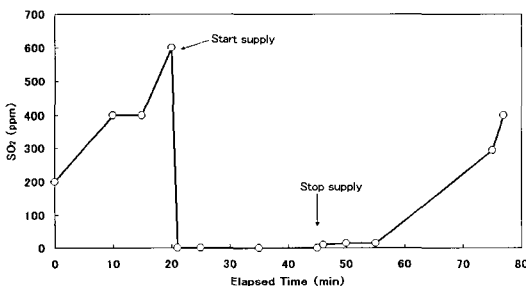


Fig. 12 The Effect of Reducing SO_2 with a Two-Towered Scrubber (electrolyzed fluid)

Even with the seawater was enough for the treatment. In cases where the water flow was stopped, the treatment continues

as the seawater rested in the filter. Fig. 12 shows how efficient the treatment is after the electrolyzed seawater passes through both sides of anode(pH 2.6) and cathode(pH 9.8) fluids. After starting sending the fluid, the speed of SO_2 treatment was faster in case of the electrolyzed fluid compare to seawater only.

5. Conclusion

Considering the effects that the atmospheric contamination materials discharged from vessels influence on shore, measures against NO_x discharged from vessels sailing within coastal areas are urgently needed.

In building up a system to reduce those materials by electrically decomposing the seawater, the experiments of the efficiency to reduce NO_x with a small tabled electrolysis and a two-towered scrubber resulted in the following.

(1) The detector for measuring the density of NO_x is aged by the chlorine gas(Cl_2), with its life being reduced. A copper granule(0.2~0.9mm and 40~80 mesh) filter is appropriate for preventing this.

(2) The experiment of the two-towered scrubber showed that NO was reduced by 90% as it was oxidized due to the chlorine or hypo-chlorine acid in acid solution by the electrolysis of seawater. It would be enough that the fluid which the scrubber sends is about 1/6 of the flux of gas. However, although it was the same acid solution, in case the chlorine is generated, NO was not reduced. The

chlorine took an important role.

(3) In reducing SO₂ by a two-towered scrubber, it was reduced by 100% with seawater only without electrolyzing the water. The desirable quantity to send the seawater was about 1/4 of the flux of the vessel gas but the treatment speed could be increased with the alkaline water being used.

References

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Author Profile



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He received B.S. Degree in Engine Department from Mokpo National Maritime Univ. and M.S. degree in Engine Department from Korea Maritime Univ. He is currently in the Ph.D. course in Ocean Mechanical & Energy Engineering from Kobe Univ. in Japan. His research interest are PM Formation-Decomposition and Combustion Characteristics