Journal of the Korean Society of Marine Engineering, Vol. 34, No. 3, pp. 399~406, 2010(ISSN 1226-9549)

Degradation and Neutralization of Total Residual Oxidant (TRO) in the Treated Ballast Water by Ozonation

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(Received October 13, 2009; Revised February 12, 2010; Accepted April 27, 2010)

Abstract : The aims of this study are to provide data on the ozone dosage control system and TRO sensor performance, to assess the performance of the degradation of total residual oxidant (TRO) neutralizer and to provide data on degradation rates of TRO in the ballast tanks, following treatment by the Ozone BWTS. This study includes the results of an evaluation of the TRO neutralizer, which was tested on the test barge. Accordingly, it has undertaken the evaluation of TRO degradation rates following treatment by the Ozone BWTS.

Key words : Ballast Water, TRO, Ozone, Ozonation, Neutralization

1. Introduction

The ozone ballast water treatment system (Ozone BWTS) treats ballast water during uptake at the start of the voyage. The ozone and bromine/bromide by products collectively know as Total Residual Oxidants (TRO) disintegrate extremely rapidly (seconds, hours or days depending on the compound). It is therefore highly unlikely that there will be any TROs remaining in the ship's ballast after a typical voyage of several days to weeks. This will ensure that there is no pollution of receiving waters, when the treated ballast water is discharged. It believes that testing demonstrates that effluent from the Ozone BWTS does not pose a threat to the receiving environment, in terms of residual chemicals and eco toxicity. In order to provide absolute surety in this regard, it will be opted to include a TRO neutralizer as part of the standard design of the system. This study therefore also includes the results of an evaluation of the TRO neutralizer, which was tested on the test barge in 2008. Accordingly, It has undertaken the evaluation of TRO degradation rates following treatment by the Ozone BWTS. The aims of this study are to provide data on the ozone dosage control system and TRO sensor performance, to assess the performance of the TRO neutralizer and to provide data on degradation rates of TRO in the ballast

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tanks, following treatment by the Ozone BWTS.

2. Materials and Methods

2.1 Testing Scheme

The Test scheme for ozone control and TRO decay indicated in **Table 1**. Total 17 cycles of tests were carried out to confirm the by products and decay TRO in the ballast water of Busan port and Nakdong river estuary.

Table 1: Test scheme for ozone control and TRO decay.

Test cycle	Test site	Salinity (PSU)	The purpose of tests
1	Busan Port	32.5	By-products (Day 0, 2, 5)
2	NakdongEstuary	17.0	TRO Decay
3	Busan Port	33.3	By - products Ecotoxicity
4	Nakdong Estuary	15.0	TRO Decay
5	Nakdong Estuary	17.0	Normal operation – corrosion
6	Nakdong Estuary	21.0	By - products (Day 0, 2, 5)
7	Nakdong Estuary	23.0	Normal operation – corrosion
8	Nakdong Estuary	21.0	By-products Ecotoxicity
9	Busan Port	31.5	Normal operation – corrosion
10	Busan Port	32.5	TRO Decay
11	Busan Port	33.0	TRO Decay
12	Busan Port	34.0	Neutralizing
13	Busan Port	33.0	Neutralizing
14	Busan Port	33.0	Ozone dose control
15	Busan Port	32.0	Neutralizing
16	Busan Port	33.0	Neutralizing
17	Busan Port	32.0	Ozone dose control

2.2 Sampling and Analytical Methods

Analysis of Ozone was undertaken on site automatically by using of installed ozone concentration analyzer (HC 500 ozone Monitor and Transmitter, WEDECO) in Ozone BWTS. The measured level was presented as automatically calculated Ozone which is equivalent to gram per normal cubic meter.

Level of TRO was measured on site automatically by using of installed TRO concentration analyzer (CL17 Chlorine Analyzer, HACH) installed separately in the ballast pipe and ballast tank the test barge, and manually by using of portable TRO concentration analyzer (DR 2500, HACH). The measured level was presented as TRC equivalent of mg/L as Cl_2, and the level of TRO was calculated as mg/L as Br_2 (1 mol Cl2=0.44 mol Br_2).

The manual determination of TRO levels was carried out in situ. Water samples were taken from the land based treatment system (mobile test barge) at appropriate time points during the five days storage following treatment. Water samples were drawn into in a brown glass bottle after washing with sample water. Determination of TRO was conducted immediately according to the DPD (N,N diethyl p phenylenediamine) colorimetric method based on USEPA 330.5 (HACH method 8167).

The analytical laboratory service for the measurement of residual chemicals (disinfection by products or DBPs) was provided by SGS Testing Korea Co. Ltd (SGS) in Anyang. Water samples were drawn directly into the pre labelled sample containers which SGS provided, including the required preservative for each parameter. The collected samples and custody documentation were cooled immediately in an ice box to 4±2℃ and transported to the test facility of SGS.

Analytical methods for each chemical are summarized in **Table 2**, and are described in more detail in the relevant Study Plans, according to the procedures in the Quality Assurance Project Plan (QAPP).

Table 2: Summary of analytical methods used for each chemical.

	Method	Unit	MDL	PQL	Remark
Bromate ion	IC Method	μg/L	0.0043	0.2	EPA Method
Trichloromethane	Liquid-Liquid Extraction GC Method	μg/L	0.73	2.0	Standard Method 8260B
Dibromochloromethane	Liquid-Liquid Extraction GC Method	μg/L	0.76	2.0	Standard Method 6232B
Bromodichloromethane	Liquid-Liquid Extraction GC Method	μg/L	0.68	2.0	Standard Method 6232B
Tribromomethane	Liquid-Liquid Extraction GC Method	μg/L	0.63	2.0	Standard Method 6232B
Monochloroacetic acid	GC Method	μg/L	0.2	0.6	EPA Method 552.2
Dichloroacetic acid	GC Method	μg/L	0.2	0.6	EPA Method 552.2
Trichloroacetic acid	GC Method	μg/L	0.2	0.6	EPA Method 552.2
Bromochloroacetic acid	GC Method	μg/L	0.2	0.6	EPA Method 552.2
Dibromoacetic acid	GC Method	μg/L	0.2	0.6	EPA Method 552.2

2.2 Ozone BWTS

Test of TRO decay was undertaken on site by using of installed the ozone based ballast water treatment system (NKOZ 010, NK Co., Ltd.). The injection level of ozone concentration was 2.5 gram of ozone per cubic meter of ballast water.

3. Results and Discussions

3.1 TRO degradation

The data from Test Cycles 1, 2, 3, 4, 6, 7, 10 and 11 were used to evaluate the TRO degradation rates and the results are presented in Figures 9, 10, 11 and 12. The test result shows the constants for the exponential decay of TRO shown in **Figure 1 & 2 and 3 & 4** respectively.

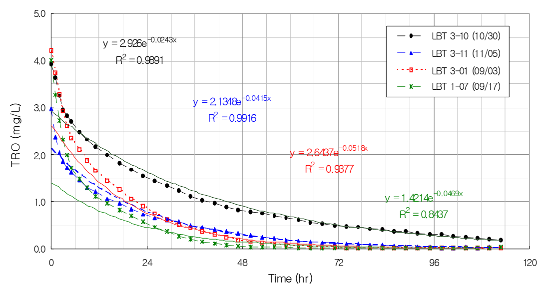

Figure 1: Decay in TRO concentrations (mg/L as Br2) over a 5 day period for Test Cycle 3-1, 1-7, 3-10 and 3-11.

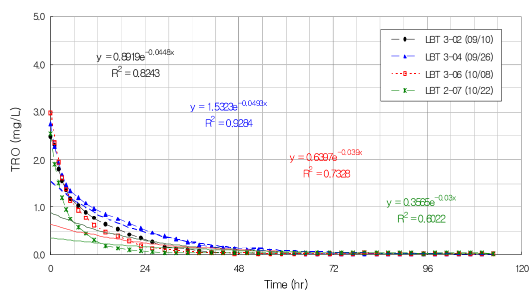

Figure 2: Decay in TRO concentrations (mg/L as Br2) over a 5 day period for Test Cycle 3-2, 3-4, 3-6 and 2-7.

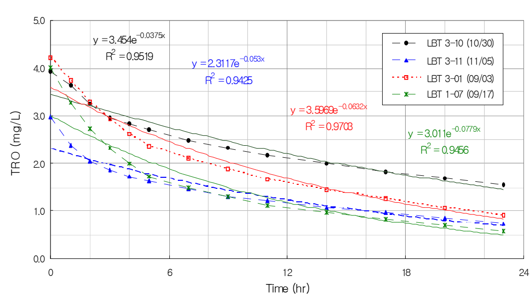

Figure 3: Decay in TRO concentrations (mg/L as Br2) over a 2 day period for test cycle 3-1, 1-7, 3-10 and 3-11.

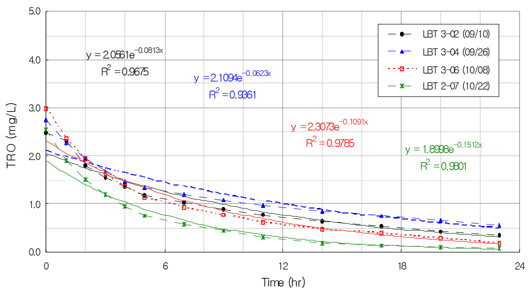

Figure 4 : Decay in TRO concentrations (mg/L as Br2) over a 2 day period for test cycle 3-2, 3-4, 3-6 and 2-7.

The data presented above indicate that the influent ballast water passed the ozone injector creating a sharp increase in TRO concentration, with initial concentrations reaching 2.48 ~ 4.23 mg/L as Br2 depending on water condition. All TRO concentrations in the ballast tanks declined over time (logarithmic rate of decay 0.038 ~ 0.151 hr 1, half life: 2.75 ~ 14.57 hr).

The maximum TRO levels measured were 4.23 mg/L at T0, 0.84 mg/L at T2 and 0.19 mg/L at T5

Some variability in degradation rates was observed between Test Cycles. Reasons for variability in degradation rates most likely relate variable seawater conditions. Only one test result performed with clean seawater on Test Cycle 10 showed a concentration of 0.19 mg/mL of TRO at de ballasting after 5 days tank holding. However, the differences in source water condition and treatment method discussed in above test result can account for the lower half life and rapid decay TRO of Ozone BWTS.

3.2 Evaluation of TRO neutralizer

Thiosulfate (S2O32−) is an oxyanion of sulfur produced by the reaction of sulfite ions with elemental sulfur in boiling water. Thiosulfate occurs naturally in hot springs and geysers, and is produced by certain biochemical processes. It instantly dechlorinates water, and is notable for its use to halt bleaching in the paper making industry. Thiosulfate is also useful in smelting silver ore, in producing leather goods, and to set dyes in textiles. Sodium thiosulfate was widely used to fix black and white photography negatives after the developing stage.

Thiosulfates reacts with halogens differently, which can be attributed to the decrease of oxidizing power down the halogen group: (http://en.wikipedia.org/wiki/Thiosulfate)

$$S_2O_3^{2-}(aq) + 4Br_2(aq) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 8Br^-(aq) + 10H^+(aq) \qquad (1)$$

$$S_2O_3^{2-}(aq) + 4Cl_2(aq) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 8Cl^-(aq) + 10H^+(aq)$$

Thiosulfate is used in the TRO neutralizer in the Ozone BWTS. The lab scaled test was conducted to evaluate the relationship of TRO and thiosulfate in the Ozone BWTS (test cycle 9 & 10).

The lab scaled test procedure was as follows;

· Collect treated ballast water samples in several flasks of 500mL

· Inject neutralizer into the samples in different neutralizer dose ratio(0~0.7) and shake gently

· Measure TRO using by TRO meter (Pocket colorimeter II, Hach)

· Neutralizer dose ratio = Neutralizer concentration (mg/L)/TRO (mg/L) (Theoretical neutralizer dose ratio is about 0.18. (= 112.1 / (4 x 159.8))

The test results are presented in **Figure 5** and **Figure 6**. The TRO proportionally decreased as according to the neutralizer dose ratio increased until ratio 0.175, and TRO concentration decreased about 0.5 mg/L and removal rate is 64 ~ 88 % at ratio 0.175. After neutralizer dose ratio 0.175, TRO neutralizing is slow. Finally, TRO neutralization completed at neutralizer dose ratio 0.44.

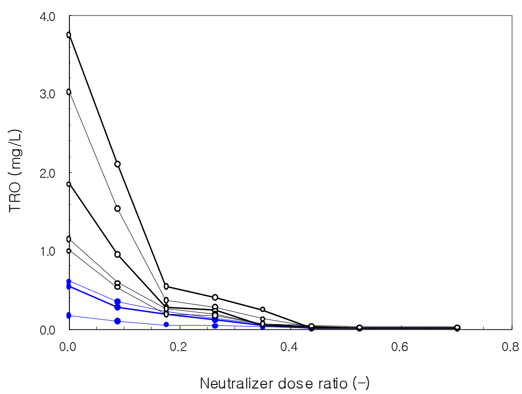

Figure 5: TRO Vs. neutralizer dose ratio at several different TRO. (Test Cycle 9 & 10)

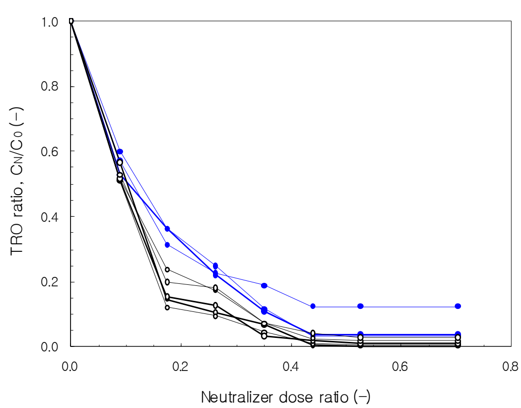

Figure 6 : TRO ratio, CN/C0Vs. neutralizer dose ratio at several different TRO. (Test Cycle 9 & 10)

Based on these results, the applied neutralizer dose ratio set point for the Ozone BWTS is set at 0.5 as designed criteria. Also neutralizer dose ratio will be changed according to TRO after neutralizer injection.

The data from Test Cycles 12 to 16 were used to evaluate the TRO neutralizer and the results are presented in **Figure 7** and **8**. The results show that TRO levels are significantly reduced by the neutralizer.

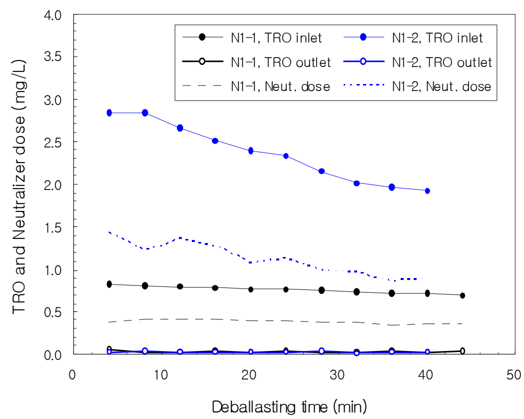

Figure 7: TRO inlet (before neutralizer injection), TRO outlet (after neutralizer injection) and neutralizer dose Vs. deballasting time. (Test Cycle 12 & 13)

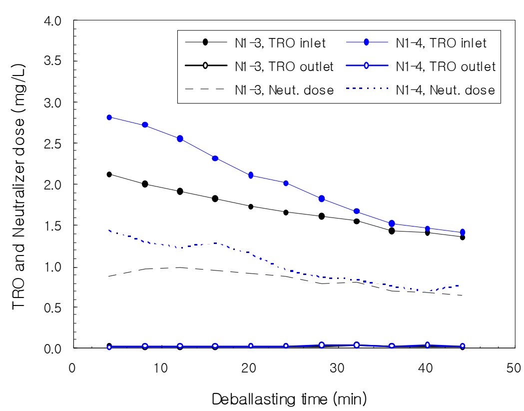

Figure 8: TRO inlet (before neutralizer injection), TRO outlet (after neutralizer injection) and neutralizer dose Vs. deballasting time. (Test Cycle 15 & 16)

As presented in **Figure 7** and 8, neutralizer dose is controlled effectively according to varied TRO over whole deballasting time and all test cycle. After neutralizer injection, TRO decreased below 0.06 mg/L (average 0.03 mg/L) irrespective of TRO inlet.

As presented in **Figure 9** neutralizer dose proportionally increased according to TRO inlet. Also neutralizer dose ratio was from 0.42 to 0.55 (average. 0.49). When TRO inlet is low relatively, neutralizer dose ratio is little high relatively. And these are same results as previously lab test.

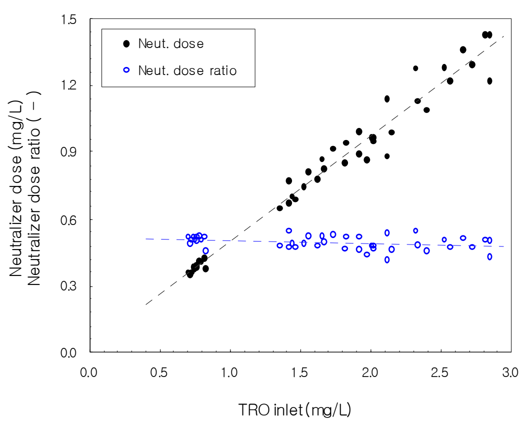

Figure 9: Neutralizer dose and dose ratio Vs. TRO inlet. (Test Cycle 12, 13, 15 and 16)

Table 3: Average TRO levels before and after TRO Neutralizer during deballasting

Test Cycle	Ballast flow-rate (m3/hr)	TRO Inlet (mg/ℓ)	TRO Outlet (mg/ℓ)	Neut. Conc (g/ℓ)	Neut. flow-rate (ℓ/min)	Neut. Dose (mg/ℓ)
12 1)	221	0.76	0.04	2.50	0.57	0.38
13 2)	217	1.69	0.03	10.00	0.30	0.83
15 3)	222	2.36	0.03	10.00	0.42	1.12
16 4)	220	2.04	0.03	10.00	0.37	1.02

1) Water samples obtained at 24 hours after ballasting

2) Water samples obtained at immediately after ballasting

3) Water samples obtained at 6 hours after ballasting

4) Water samples obtained at immediately after ballasting

Table 4: Concentration of DBPs before and after TRO Neutralizer.

Active Substance and Relevant Chemicals	Unit	MDL	Test Cycle N1 – 3D			Test Cycle N1 – 4D		
			Control	Before	After	Control	Before	After
Bromate ion	μg/L	0.0043	N.D	N.D	N.D	N.D	N.D	N.D
Monochloroacetic acid	μg/L	0.07	N.D	2.97	1.04	N.D	1.69	0.740
Dichloroacetic acid	μg/L	0.14	N.D	N.D	N.D	N.D	N.D	N.D
Trichloroacetic acid	μg/L	0.04	N.D	N.D	N.D	N.D	N.D	N.D
Dibromoacetic acid	μg/L	0.02	N.D	4.41	1.35	N.D	4.01	0.950
Bromochloroacetic acid	μg/L	0.02	N.D	N.D	N.D	N.D	N.D	N.D
Trichloromethane	μg/L	0.73	N.D	N.D	N.D	N.D	N.D	N.D
Dichlorobromomethane	μg/L	0.68	N.D	N.D	N.D	N.D	N.D	N.D
Dibromochloromethane	μg/L	0.76	N.D	N.D	N.D	N.D	N.D	N.D
Tribromomethane	μg/L	0.63	N.D	25.4	19	N.D	22.8	9.70

ND = Not Detected

Chemical analysis is conducted for evaluation relationship between neutralization and DBPs; relevant chemicals and neutralizer, and the results from test cycle 15 & 16 are presented in Tables 6. Neutralization results in reducing of DBPs. We believe that thiosulfate neutralizes the brominated DBPs and consequently reduces the risk of Ozone BWTS.

For most DBPs, none were detected in the control nor the before and after neutralizer samples. For those chemicals that were detected in samples before neutralizer, these were reduced substantially following neutralization. It is clear that the neutralizer is effective at removing any risk to the receiving environment from possible residual DBPs.

4. Conclusions

The test results indicate that the TRO sensors linked to the Ozone BWTS monitoring and control system are an effective method for managing ozone dosage, to keep TRO levels in treated influent ballast water below a maximum set level. Most importantly this system is effective for controlling neutralizer feed to keep TRO levels in the ultimate ballast water discharge below the PNEC level of 0.1 mg/L.

In response to safety concerns, the system design and operating procedure has been amended to include redundant pairs of TRO sensors at each TRO sensor point, and provide for complete system shut down in the highly unlikely event that any pair of TRO sensors fails.

While we believes that the TRO testing demonstrates that effluent from the Ozone BWTS does not pose a threat to the receiving environment, in terms of residual chemicals and eco toxicity, in order to provide absolute surety in this regard, it will be opted to include a TRO neutralizer as part of the standard design of the system. The evaluation of the TRO neutralizer presented in this report indicates that it is very effective at reducing TRO and individual DBP levels.

The results presented in this study indicate that TRO degradation rates in ballast tanks following treatment by the Ozone BWTS are rapid.

One result of our test performed with clean seawater on Test Cycle 10 showed a concentration of 0.19 mg/mL of TRO at de ballasting after 5 days tank holding with 14.57 hr of half life, which is comparable with other applications and calculated concentration. However, the differences in source water condition and treatment methods discussed above can account for the discrepancy of TRO decay between Ozone BWTS and other applications and data from open literature using ozone to treat water with high organic content.

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