The U.S. Naval Research Laboratory (NRL) and Pearl Harbor Naval Shipyard (PHNSY) Chlorination/Dechlorination System Project: Evaluation of Chemical Agents

Midshipman 1/C John Patrick Caniban, USN, Class of 2019

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Abstract

The U.S. Naval Academy (USNA) worked with the U.S. Naval Research Laboratory and Pearl Harbor Naval Shipyard to improve pierside Chlorination Unit (CU) systems to increase the efficiency in controlling biofouling of submarine seawater cooling systems. Studies were performed to better understand optimal chlorine levels for biofouling reduction and to evaluate the efficacy and potential toxicity of alternative dechlorination agents, sodium thiosulfate ($Na_2S_2O_3$) in place of sodium metabisulfite ($Na_2S_2O_5$), to ensure system effluent meets regulatory requirements for discharge.

Laboratory Chemical Agent Evaluation and Acute Toxicity Studies

Hendrix Oceanography Laboratory, U.S. Naval Academy, Annapolis, MD

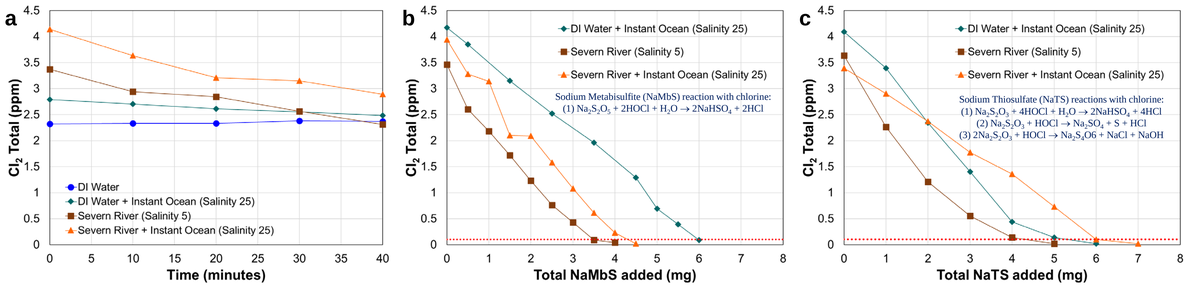

Figure 1. (**a**) Cl_2 Total concentration (ppm) stability vs. time for 4 different "challenge" waters; (**b**) Cl_2 Total concentration (ppm) vs. total weight of sodium metabisulfite (NaMbS) titrated into a chlorinated 1 L solution and (**b**) Cl_2 Total concentration (ppm) vs. total weight of sodium thiosulfate (NaTS)titrated into a chlorinated 1 L solution. Chlorine concentrations were measured using a *Hach SL1000 - PPA Portable Parallel Analyzer- Portable Colorimeter* with *Chemkey* reagents. The red dashed line indicates the PHNSY regulatory discharge limit of < 0.1 ppm Cl_2 Total.

Clorox Regular Bleach (Concentrated, 6% Sodium Hypochlorite) was used to chlorinate 4 different "challenge" waters to 2-5 ppm total chlorine (Cl_2 Total): de-ionized (DI); DI water plus "Instant Ocean" (salinity ~ 25), Severn River water (salinity ~ 5), and Severn River water plus "Instant Ocean" (salinity ~ 25). Chlorinated waters were checked for stability over time. Severn River challenge water showed significant rapid loss of chlorine over time, likely due to reactions with organic matter (**Fig. 1a**). All chlorinated challenge waters except DI water were titrated with sodium metabisulfite (NaMbS; **Fig. 1b**) and sodium thiosulfate (NaTS, **Fig.1c**) to estimate the weight-to-weight ratio (dechlorination agent-to-chlorine) required to reduce Cl_2 Total below the PHNSY regulatory discharge limit of < 0.1 ppm. Results suggest a dechlorination agent-to-chlorine weight ratio of ~1-1.4 and ~1-1.5 for NaMbS and NaTS, respectively, is required to dechlorinate challenge waters to < 0.1 ppm Cl_2 Total. This suggests that both agents effectively dechlorinate challenge waters. Acute toxicity (mortality) testing was performed on *Artemia* (brine shrimp; **Fig. 2a**) to investigate optimal chlorine levels for anti-biofouling and potential acute toxicity related to use of NaMbS or NaTS as dechlorination agents. Briefly, *Artemia* were hatched and grown in three separate growth tanks filled with Severn River water plus "Instant Ocean" (salinity ~ 25). After maturation of larvae, a sub-sample was drawn from each growth tank and treated with either chlorinated challenge water, or chlorinated challenge water that had been dechlorinated with NaMbS or NaTS at the threshold dechlorination agent-to-chlorine weight ratio (1 X) or at overburdened weight ratio (2 X) . After 5 minutes, three samples were drawn from each treatment sub-sample and counted for live vs. dead organisms (**Fig. 2b**). Only the treatments of 2.0 ppm Cl_2 Total and 4.0 Cl_2 Total showed any significant *Artemia* mortality and in these treatments, mortality was < 15% (**Fig. 2c**).

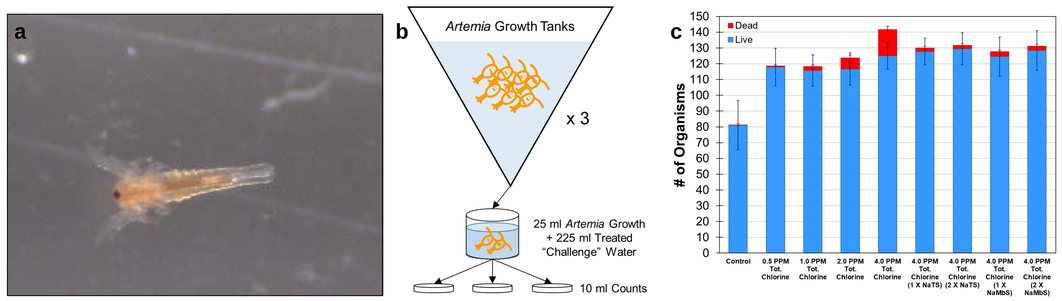

Figure 2. (**a**) Picture of a brine shrimp (*Artemia*) under the counting microscope, (**b**) experimental set-up for acute toxicity (mortality) studies using treated Severn River water plus "Instant Ocean" (salinity ~ 25) and (**c**) results of the acute toxicity (mortality) testing.

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Chlorination/Dechlorination System Mock-Up Testing

Center for Corrosion Science & Engineering, U.S. Naval Research Laboratory, Key West (NRL-KW), FL

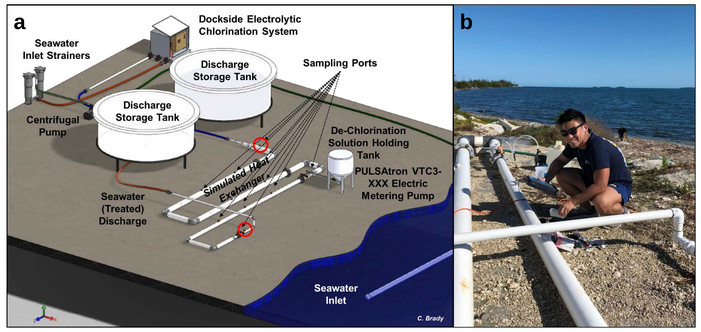

Figure 3. (**a**) Diagram of chlorination/dechlorination system mock-up used in testing at NRL-KW and (**b**) Midshipman 1/C J. P. Caniban testing Free and Total Cl_2 concentrations in dechlorinated system effluent using a *Hach SL1000 - PPA Portable Parallel Analyzer- Portable Colorimeter*. The system mock-up was designed to simulate dockside electrolytic CU systems used at PHNSY. It draws in local seawater through seawater inlet strainers into an electrolytic chlorinator (CU). Chlorinated seawater is then passed through piping designed to submarine seawater cooling systems. There are multiple sampling points to monitor chlorine concentrations through the system. Prior to discharge, a diaphragm injection pump is used to add a dechlorination agent with a known concentration at a fixed (but adjustable) flow rate. Seawater was ~ 27 °C with a salinity of 36 during testing from 26-28 February 2019.

Figure 3 shows the chlorination/de-chlorination system used in testing at NRL-KW from 26-28 February 2019. System chlorination levels were maintained at ~3-6 mg/L (ppm Cl_2 Total) and dechlorination agent was added at a fixed flow rate prior to discharge. Dechlorination agent concentration was systematically lowered towards a threshold weight ratio of de-chlorination agent to chlorine of 1.29 to 1.63 for $Na_2S_2O_3$ and > 1.39 for $Na_2S_2O_5$ needed to meet the PHNSY regulatory discharge limit of < 0.1 ppm Cl_2 Total (**Table 1**). Results support a conclusion that $Na_2S_2O_3$ is a suitable alternative to $Na_2S_2O_5$ to dechlorinate seawater chlorinated up to ~ 5 ppm.

Table 1. Results of chlorination/dechlorination system testing conducted at NRL-KW, 26-28 February 2019. Green indicates Total Cl_2 concentration in discharge effluent < 0.1 ppm.

Run	Dechlor. Agent	SW Flow Rate (L/min)	In				Cl_2 Mass Addition Rate (g/min)		Dechlor. Mass Addition Rate (g/min)	Out				Dechlor./Chlor. Weight Ratio
			Cl_2 Free (mg/L)		Cl_2 Total (mg/L)					Cl_2 Free (mg/L)		Cl_2 Total (mg/L)		
			Mean	*Stdev.*	*Mean*	*Stdev.*	*Mean*	*Stdev.*		*Mean*	*Stdev.*	*Mean*	*Stdev.*	
1	*No Dechlor.*	163	3.84	0.03	3.96	0.07	0.66	0.01	0.00	3.73	0.11	3.96	0.05	N/A
2	*Sodium Thiosulfate*	167	4.07	0.38	4.15	0.48	0.71	0.07	5.06	0.01	0.00	0.01	0.01	7.21
3	*Sodium Thiosulfate*	178	4.15	0.28	4.27	0.31	0.78	0.06	2.53	0.01	0.00	0.01	0.01	3.27
4	*Sodium Thiosulfate*	178	4.14	0.24	4.27	0.14	0.78	0.03	1.27	0.01	0.00	0.02	0.00	1.63
6	*Sodium Thiosulfate*	148	4.73	0.66	4.91	0.71	0.74	0.09	0.95	0.06	0.01	0.12	0.05	1.29
5	*Sodium Thiosulfate*	178	4.21	0.20	4.40	0.20	0.80	0.02	0.63	0.14	0.03	0.21	0.04	0.79
7	*Sodium Thiosulfate*	144	5.30	0.20	5.50	0.20	0.81	0.02	0.47	0.61	0.17	0.73	0.18	0.59
8	*Sodium Metabisulfite*	155	5.54	0.20	5.74	0.20	0.91	0.02	1.27	0.14	0.17	0.20	0.23	1.39
9	*Sodium Metabisulfite*	151	4.24	0.20	4.26	0.20	0.66	0.02	0.63	2.00	0.20	2.11	0. 20	0.96

Chlorination/Dechlorination System Drydock Testing

Pearl Harbor Naval Shipyard, Pearl Harbor, HI

Table 2. Results of chlorination/dechlorination system testing at PHNSY, 13-14 March 2019. Green indicates Total Cl_2 concentration in discharged effluent < 0.1 ppm.

Run	Type	Chlorinated ASW		Cl_2 Mass Addition Rate (g/min)		Dechlor Mass Addition Rate (g/min)	Dechlorinated Effluent		Dechlor/Chlor Weight Ratio
		Cl_2 Total (mg/L)					Cl_2 Total (mg/L)		
		Mean	*Stdev.*	*Mean*	*Stdev.*		*Mean*	*Stdev.*	
1	Sodium Thiosulfate	1.00	0.11	2.62	0.46	3.68	0.00	0.00	1.61
2	Sodium Thiosulfate	2.08	0.06	5.07	0.22	6.22	0.04	0.01	1.18
3	Sodium Metabisulfite	1.15	0.07	2.97	0.28	3.68	0.02	0.04	1.35
4	Sodium Metabisulfite	2.11	0.08	5.24	0.15	6.22	0.08	0.07	1.21

Table 2 shows the results of chlorination/dechlorination system drydock testing conducted at PHNSY, 13-14 March 2019 (**Fig. 4**). These tests used variable system chlorination levels up to ~2 mg/L (ppm Cl_2 Total) and constant dechlorination agent concentration. Dechlorinator flow rate was adjusted to achieve a dechlorination agent to chlorine weight ratio of ~1.2 or greater. Results showed that above this ratio, both $Na_2S_2O_3$ and $Na_2S_2O_3$ provided dechlorination that met the PHNSY regulatory discharge limit of < 0.1 ppm Cl_2 Total, even at system Cl_2 concentrations up to 2 mg/L (ppm Cl_2 Total).

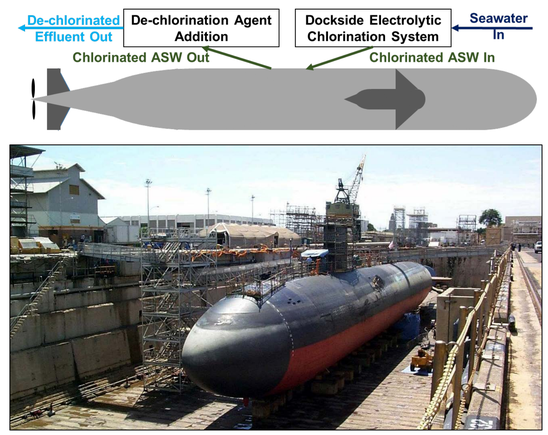

Figure4. Conceptual diagram of chlorination/dechlorination system flow during drydock testing at PHNSY, 13-14 March 2019. Photo is a DoD stock photo of the *USS Greeneville* (SSN-772) in Dry Dock #1 at the PHNSY and Intermediate Maintenance Facility (IMF), Pearl Harbor, Hawaii, on Feb. 21, 2001 (UNI News, December 20, 2018).

Conclusions: ***Sodium thiosulfate (NaTS) is an effective dechlorination agent for chlorine levels up to 2 ppm Cl_2 Total in submarine seawater cooling systems when used in a > 1.2 weight ratio of dechlorination agent-to-chlorine. Even with significant overburden NaTS, no significant acute toxicity to Artemia was noted. Results support NaTS as an alternative to sodium metabisulfite in shipyard chlorination/dichlorination systems but studies should continue to evaluate potential chronic toxicity to other organisms and other potential effects on shipboard systems.***