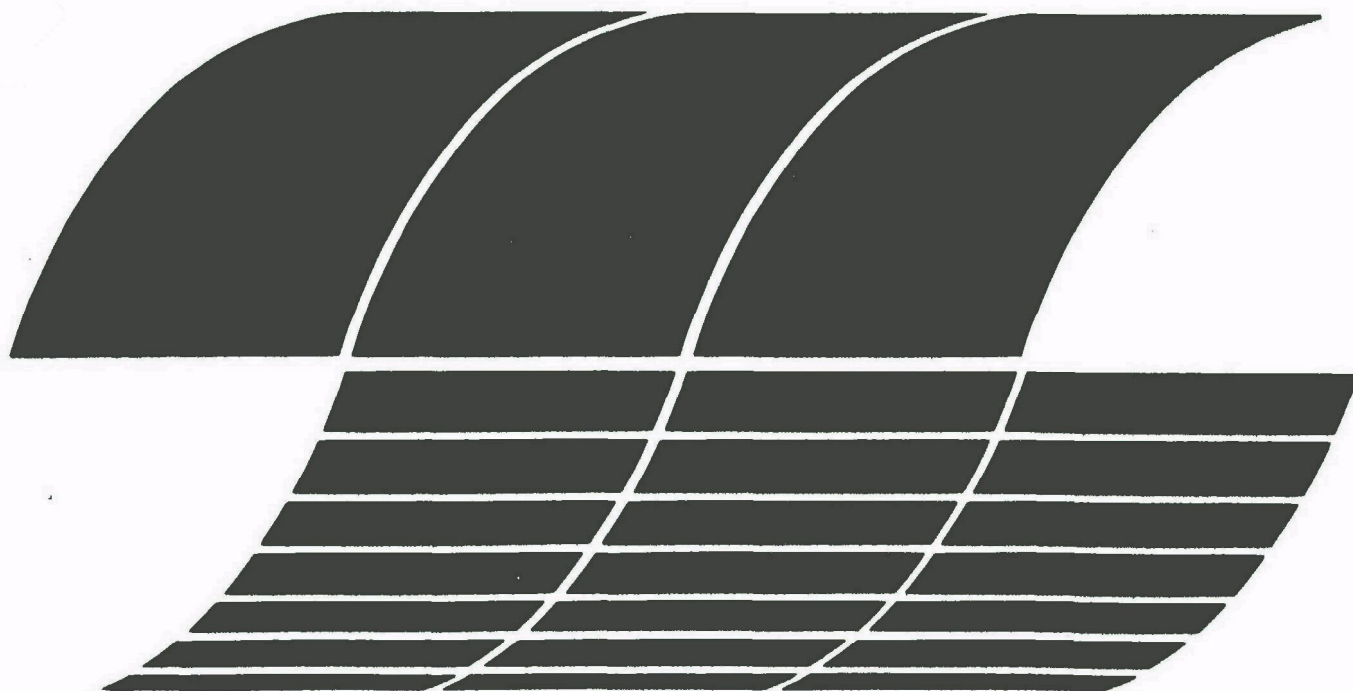




# **Residual Oxidants Removal from Coastal Power Plant Cooling System Discharges: Field Evaluation of SO<sub>2</sub> Addition System**

**Interagency  
Energy/Environment  
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# **Residual Oxidants Removal from Coastal Power Plant Cooling System Discharges: Field Evaluation of SO<sub>2</sub> Addition System**

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## ABSTRACT

This study was conducted to evaluate the performance of a dechlorination system which uses sulfur dioxide to remove residual oxidants from chlorinated sea water in a power plant cooling system. Effectiveness of removal and development of average and maximum achievable levels of dechlorination were to be developed. A field sampling and analysis program at Pacific Gas and Electric's Potrero power plant, located in San Francisco, was developed to provide the necessary data. Samples of unchlorinated, chlorinated, and dechlorinated cooling water were obtained at the plant. These samples were collected during 28 sampling periods -- 14 at flood tide and 14 at ebb tide conditions -- and analyzed for several chemical and physical constituents. An amperometric titrator was used for field analysis of total oxidant residual (TOR) and free oxidant residual (FOR). Analytical results, along with plant operating data and laboratory experiments, provided the information used to evaluate the dechlorination system. Major conclusions which can be derived from the data are as follows: (1) the dechlorination system studied showed effective removal of residual oxidants from chlorinated sea water used in the power plant cooling system; (2) the dechlorination system proved reliable as no measurable oxidant residual was found at the effluent outfall; and (3) due to the effectiveness of the dechlorination system in removing all measurable oxidant residual, average and maximum levels of dechlorination cannot be determined.

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## LIST OF ABBREVIATIONS AND SYMBOLS

PG&E	- Pacific Gas and Electric Company
TOR	- Total Oxidant Residual
FOR	- Free Oxidant Residual
COR	- Combined Oxidant Residual
SO <sub>2</sub>	- Sulfur Dioxide
BOD	- Biological Oxygen Demand
TOC	- Total Organic Carbon
D.O.	- Dissolved Oxygen
MW	- Megawatt
DC	- Dechlorinated Sample
C	- Chlorinated Sample
RW	- Unchlorinated Sample

## SECTION 1

### INTRODUCTION

Chlorination of cooling waters is the most successful and widely applied method presently used to control biofouling of condensers in power plant cooling circuits. Recently, some power plant chlorination practices have been revised to include dechlorination of cooling water prior to discharge into surface waters. Dechlorination results in the removal of chlorine residuals, and may have a significant impact on future chlorination practices.

Current chlorination practices require the addition of a specified quantity of chlorine at the cooling water intake. The chlorine dosage is presently limited by the residual chlorine (residual oxidant in the case of sea water) that is found downstream of the cooling cycle in the outfall. Federal standards require that the residual chlorine/oxidant level cannot exceed 0.5 mg/l at any time and cannot exceed an average of 0.2 mg/l for a period of two hours in any day from any one unit (1). Many state and local standards are more stringent than the federal standards. Dechlorination prior to discharge of chlorinated cooling water can assist plants in conforming with the more stringent standards.

This report was prepared under the direction of EPA to provide valuable data necessary for evaluating the performance of a dechlorination system designed to remove residual oxidants from chlorinated sea water. Evaluation of dechlorination practices was accomplished by development of this program consisting of sample collection for unchlorinated, chlorinated and dechlorinated streams and performance of physical and chemical analysis for relevant parameters. Analysis was performed for several constituents in each sample immediately after this sampling period. Analyses results from 28 sample periods, for the three streams mentioned above, along with plant operating data and laboratory experiments, provided the information used to evaluate the dechlorination system.



Pacific Gas and Electric's Potrero power plant (located in San Francisco, California) is currently operating a full scale sea water de-chlorination system on a daily basis and was thus selected for this field sampling study.

## SECTION 2

### CONCLUSIONS AND RECOMMENDATIONS

This section highlights the conclusions reached in this study and presents recommendations for further research.

#### CONCLUSIONS

- Analytical data obtained during the course of this study show that dechlorination is a reliable and effective method of removing residual oxidants from chlorinated sea water used in power plant cooling circuits. Specifically, sulfur dioxide was shown to be effective in removing residual oxidants at levels near 0.2 mg/l from chlorinated sea water at PG&E's Potrero power plant.
- Results of amperometric titration showed no measureable oxidant residual at the outfall during the 28 sampling periods.
- Based on residual oxidant measurements, it is concluded that there is no tidal effect on dechlorination at the Potrero power plant.
- The effects of organic loading could not be determined at the Potrero power plant because of extremely low organic loading as indicated by BOD and TOC measurements.
- Results obtained from laboratory tests suggest that dechlorination efficiencies tend to increase with increasing temperature. However, it appears that this increase in efficiency can be attributed to an increase of TOR decay, in the time period between chlorination and dechlorination, and not due to the dechlorination reaction.
- Due to the effectiveness of the dechlorination system in removing all measurable oxidant residual, average and maximum levels of dechlorination cannot be determined.

#### RECOMMENDATIONS

- Continued evaluation of dechlorination on sea water cooling circuits containing higher levels of organics is required in order to determine the effect of organics on dechlorination.
- Evaluate dechlorination at higher chlorine dosages to determine the effective limits of dechlorination.

### SECTION 3

#### DESCRIPTION OF THE POTRERO POWER PLANT

Information presented in the following discussion pertains to the portion of the Potrero power plant associated with the cooling water circuit, chlorination and dechlorination systems. Plant operating parameters for these systems are also presented.

#### GENERAL PLANT LAYOUT AND OPERATING PARAMETERS

The Potrero power plant is located on San Francisco Bay approximately 7 miles southeast of the Golden Gate Bridge. The power plant consists of three units; however, for this study only unit #3 was evaluated. Gross generating capacity of Unit #3 is 210 MW with a maximum cooling water flow rate of  $8.74 \text{ m}^3/\text{sec}$ . (140,000 gpm) (2).

A plot plan diagram of Unit #3 is shown in Figure 1. The diagram shows the locations of the once through cooling water circuit, turbine generator building, chlorination system and dechlorination system. Cooling water withdrawn from the bay passes through a bar rack and travelling screens to two circulating water pumps which supply cooling water to the condenser. The condenser consists of two separate unit halves, each supplied by a separate circulating water pump. Heat exchange occurs in the condensers, consisting of 22.2 mm (7/8 in) diameter aluminum-brass or copper nickel alloy tubes (2). Immediately downstream of the condenser the heated water from both halves combine and at this point is dechlorinated. Following dechlorination, the water travels to the outfall structure and is subsequently discharged into the bay.

#### Chlorination System

Chlorine is injected continuously for 30 minutes, twice daily, into each half of the cooling water circuit just upstream of the circulating water pumps. Tunnel #1 (see Figure 1) is chlorinated at 0900 and 1500 hours, followed immediately by chlorination of Tunnel #2 at 0930 and 1530 hours.

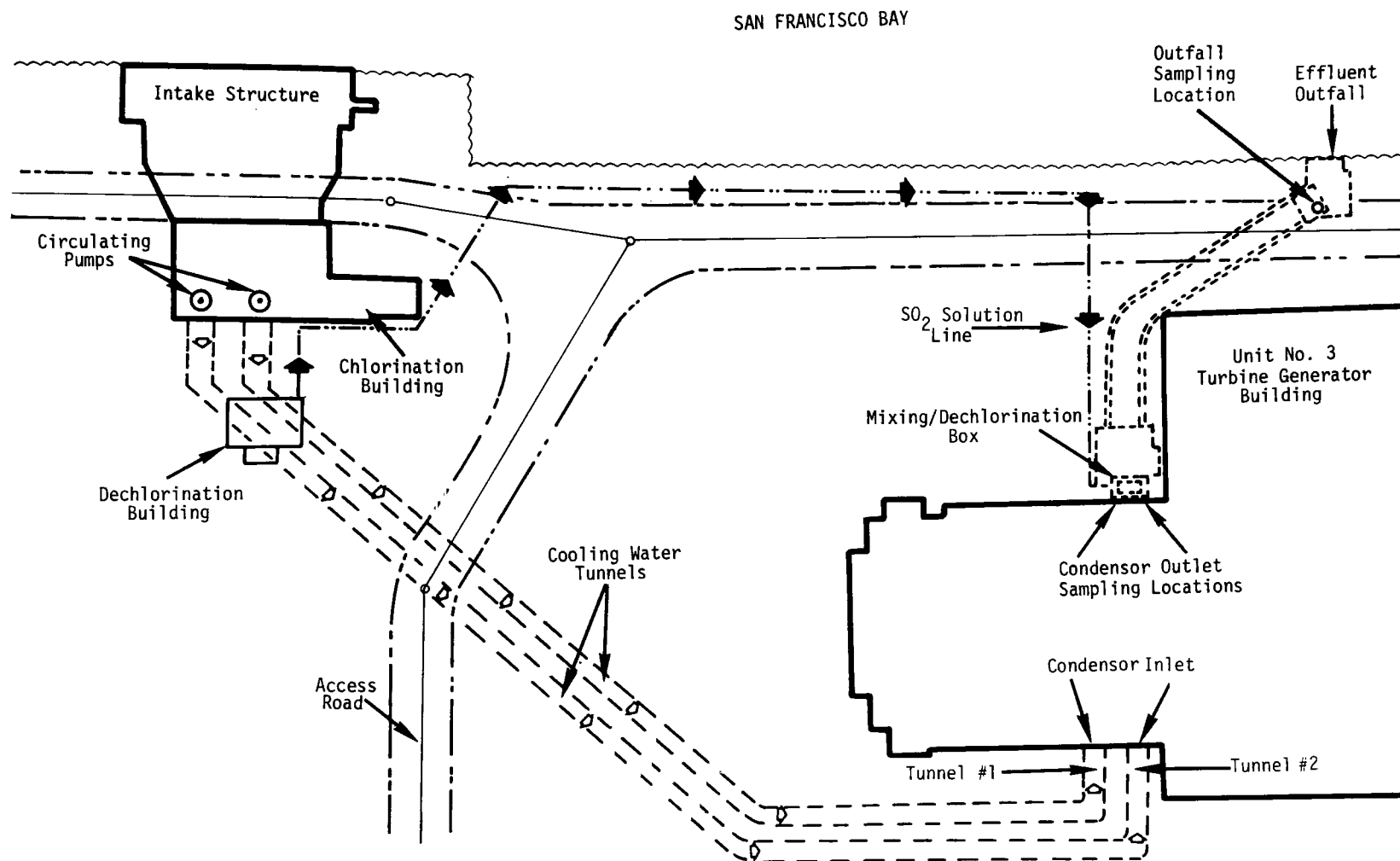


Figure 1. Plot plan diagram of the Potrero power plant.

At the Potrero plant compressed liquid chlorine is withdrawn from storage cylinders, evaporated and injected into a small stream of sea water, producing a concentrated chlorine solution. During the sampling program the concentration of this solution on the average was 130 mg/l. This solution is injected into the intake cooling water immediately upstream of each of the circulating water pumps.

Oxidant residuals are normally adjusted between 0.3 and 0.4 ppm of total oxidant residual (TOR) at the condenser inlet. This adjustment is normally performed after an extended non-use period or after repair of malfunctions in the chlorination system. The adjustment is made by measuring TOR at the condenser inlet while manually adjusting the chlorine dosage to produce the desired TOR. The approximate chlorine feed rate associated with the desired TOR (determined by PG&E) is 9.5 Kg/hr (20.8 lb/hr).

When sea water is chlorinated the principle equilibrium species formed are brominated compounds analogous to chlorinated species produced in fresh water. In the pH range from 6 to 8 these brominated species are HOBr, OBr<sup>-</sup>, NBr<sub>3</sub>, NHBr<sub>2</sub> and NH<sub>2</sub>Br (9).

### Dechlorination System

The dechlorination system employs the same principle of operation as the chlorination system with two main differences. Sulfur dioxide (SO<sub>2</sub>) is used as the dechlorinating compound and the point of addition of the concentrated SO<sub>2</sub> solution is at the mixing box located within the condenser cooling water discharge.

The dechlorination system is operated for an hour twice daily concurrent with chlorination. The dechlorinator removes total oxidant residual from mixed cooling waters of both halves of the condenser, although for the first 30 minutes only Tunnel #1 is chlorinated and the following 30 minutes only Tunnel #2 is chlorinated.

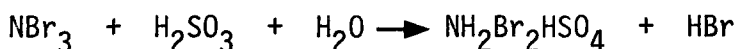
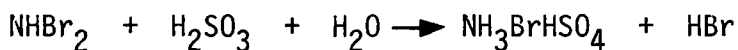
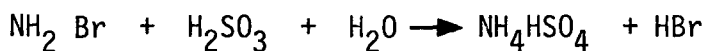
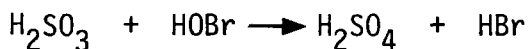
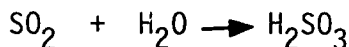
SO<sub>2</sub> is withdrawn from storage cylinders, evaporated and injected into a small stream of sea water producing an SO<sub>2</sub> solution. The average concentration of the SO<sub>2</sub> solution during the sampling program was 500 mg/l. This solution is piped to the mixing box where it is dispersed through seven diffusers into the combined chlorinated and unchlorinated streams.

Optimization of the dechlorination system is performed when residual oxidant is measured at the outfall or when the system is started up after a period of down time. Optimization is performed (by PG&E) in the following manner:

- SO<sub>2</sub> feed rate is manually increased during chlorination while holding the chlorine feed rate constant.
- Total oxidant residual is measured at the outfall as the SO<sub>2</sub> feed rate is increased.
- SO<sub>2</sub> feed rate is increased until there is no measurable TOR at the outfall.
- SO<sub>2</sub> feed rate is then increased by 50 lb SO<sub>2</sub>/24 hr as a safety factor.

The SO<sub>2</sub> feed rate determined by PG&E is 7.6 Kg/hr (16.7 lb/hr) for a chlorine feed rate of 9.5 Kg/hr (20.8 lb/hr).

When sulfur dioxide is added to the chlorinated cooling water it reacts instantaneously with the brominated species according to following equations (10):



### Sampling Points

Sampling locations are shown in Figure 1. Chlorinated and unchlorinated cooling waters were sampled at the outlet of the condenser prior to combination of the two streams in the mixing box. Both sampling points were equipped with sampling taps; however, both were under a vacuum of about 25.4 cm (10 in) of mercury. The sampling location for dechlorinated cooling water was a manhole situated downstream of the dechlorinator at the outfall structure. The sampling line was submerged in the dechlorinated effluent by using a weighted strainer.

## SECTION 4

### SAMPLING EQUIPMENT AND METHODOLOGY

The following discussion details sampling equipment and methods employed to collect samples of unchlorinated, chlorinated and dechlorinated samples of sea water from the power plant's cooling circuit. Included is the special sampling method used to collect samples for oxidant residual analysis and tests performed to determine if the sampling collection system had any effect on volatile organic compounds or dissolved oxygen.

#### SAMPLING APPARATUS

The sampling system employed in this study was designed to conform with the following design criteria:

- System must be capable of overcoming vacuum at condenser outlet sampling points and 15 feet of static head from the dechlorinated sampling point.
- Collected sample shall be shielded from sun light in order to avoid rapid decay of oxidant residuals.
- Each sample obtained during a single sampling period must be representative of the same once through cooling water whether it be unchlorinated, chlorinated and dechlorinated water.

The sampling system designed and constructed is shown in Figures 2 and 3. The system basically consists of a vacuum pump, vacuum sample collection tank, vacuum tank top with sampling control valve, and sample lines. This system was constructed in triplicate enabling identical systems to be utilized at each of the three sampling locations. The only difference between the three sampling systems was that the condenser chlorinated and unchlorinated sampling systems were attached to the existing taps on the condenser outlet; while the dechlorinated sampling system was connected to a weighted sampling strainer at the end of the sample line which was submerged in the dechlorinated effluent below the manhole.

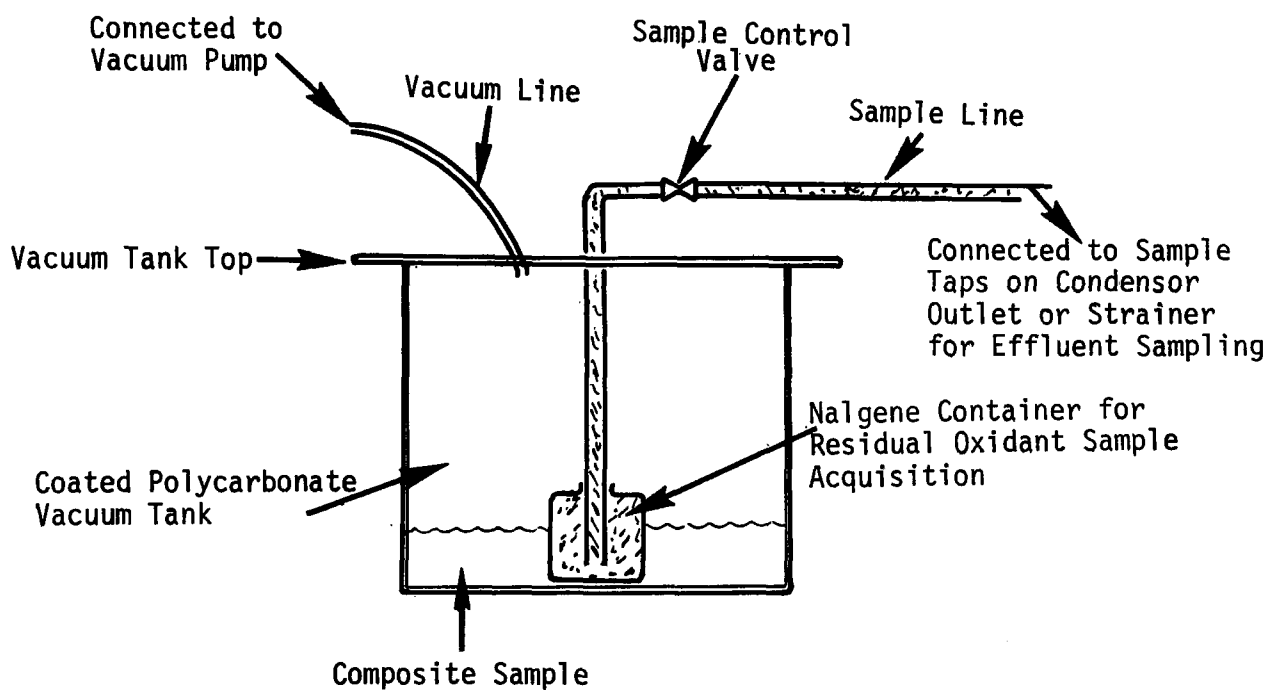


Figure 2. Vacuum sampling system



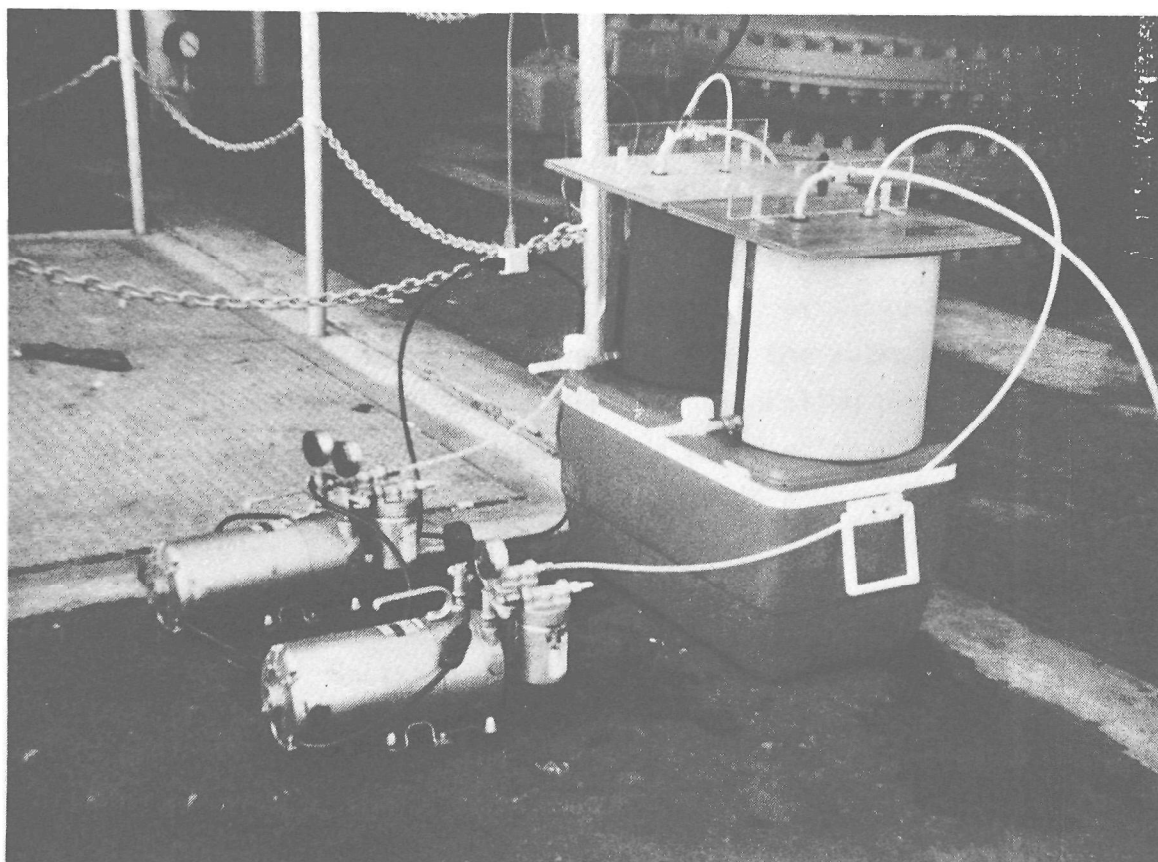


Figure 3. Chlorinated and unchlorinated sampling collection systems.

## SAMPLING SYSTEM CHECK-OUT

Following construction of the units, tests were performed to study the effect of samples, containing volatile organic compounds and dissolved oxygen, obtained with the vacuum system. In the case of volatile organics a known volume of sea water was spiked with known volumes of haloforms. The spiked solution was evacuated into the field sampling system using the vacuum pump, thus simulating field conditions. After collection, both spiked samples (before and after collection) were analyzed for volatile organic compounds. Results showed that no significant changes in organic concentrations was observed utilizing the vacuum sampling system (see Appendix A for presentation of the detailed results).

Dissolved oxygen levels of tap water were measured before and after collection with the field sampling apparatus, as discussed previously for volatile organics. Results showed that, on the average, oxygen levels declined approximately 0.25 ppm during the sampling period. This value is not considered excessive because the reported precision limit for the dissolved oxygen instrument is  $\pm 0.1$  ppm with a measurement accuracy of  $\pm 0.2$  ppm (3).

## SAMPLING AND METHODOLOGY AND RATIONALE

The program consisted of 28 sampling periods, 14 at ebb tide and 14 at flood tide conditions. (Refer to Appendix B for a detailed presentation of tide conditions existing at each sampling period). During each sampling period samples were simultaneously obtained for chlorinated, unchlorinated and dechlorinated cooling water. Consistent sampling procedures were maintained throughout the program with the exception of the first three tests which differed from the remaining 25 tests in sample acquisition for residual oxidant determination. Results of residual oxidant analysis in the first three tests were found to be unexpectedly low. This resulted from residual oxidant decay during the time period from sample collection to residual oxidant analysis. Therefore, a change in the sampling procedure was necessary to minimize sample degradation, thereby insuring a greater degree of accuracy. This objective was accomplished by the addition of a one liter nalgene container into each sampling system as shown in Figure 2. The nalgene container permitted recovery

of the most recent sample acquired to be analyzed for oxidant residuals. In the first three tests the composite sample was analyzed to determine residual oxidants. During the following 25 tests samples collected in the nalgene container containing the most recent sample acquired (not the composite) were analyzed to determine residual oxidants. The composite sample was used for all other analyses including volatile organics analyses.

The following sampling procedure was used during sampling periods 4 through 28. Procedures for periods 1, 2 and 3 were slightly different for oxidant residual sampling as mentioned above. (Times referenced to the start of the chlorination cycles.)

- (1) Prerinse of sampling system - at 10 minutes the sampling system was started at all locations. After a small quantity of liquid was collected the system was stopped and the sample discarded. All sample lines were drained of any liquid.
- (2) At 15 minutes sampling was initiated at all locations.
- (3) At 16-17 minutes the dechlorinated sampling system was turned off, the nalgene container removed, replaced by another nalgene container and the system was restarted. Immediate titration for TOR and FOR was performed. (TOR = Total Organic Residual; FOR = Free Organic Residual; FOR analysis was performed only if there is a measurable TOR).
- (4) At 19-20 minutes procedure 3 was performed on the chlorinated sample and the system was restarted.
- (5) At 24 minutes procedure 3 was performed on the dechlorinated sample, except the nalgene container was not replaced and the system was not restarted.
- (6) At 25 minutes the chlorinated and unchlorinated sampling systems were shut down. The nalgene container from the chlorinated sampling system was removed and analyzed immediately for TOR and FOR. Also a portion of the unchlorinated sample was analyzed for TOR.

The designated sampling times and procedures stated in the sampling procedure were selected for the following reasons:

- Prerinse of the sampling system was required to prevent contamination from liquids left in the lines and containers from previous sample periods.
- Initiation of the sample collection was initiated at 15 minutes to ensure the system had established equilibrium and to allow time for prerinse of all systems.

- Sample collection period of 10 minutes was to allow adequate time to collect and analyze chlorinated and dechlorinated samples for residual oxidants.
- Sampling was concluded at 25 minutes to ensure no overlap occurs between chlorination cycles of Tunnel No. 1 and Tunnel No. 2 (overlap would cause contamination of unchlorinated cooling water with chlorinated cooling water and vice versa).

## SECTION 5

### ANALYSIS METHODOLOGIES

Analysis of the cooling water samples included both field and laboratory analysis. The following is a summary of the analyses performed, analytical methods used, measurement accuracies and detection limits. A detailed discussion relative to the accuracy of residual oxidant analysis and adjustments made to increase the accuracy is also presented.

#### FIELD ANALYSIS

Immediate on-site analysis was required for the following unstable parameters: TOR, FOR, pH, dissolved oxygen (D.O.) and temperature.

TOR and FOR were determined using the Fisher and Porter portable amperometric titrator (model 17T1010). Measurement accuracy of the amperometric titration is  $\pm 0.01$  ppm of oxidant residual with a minimum detection level of 0.03 ppm (4,5,6,7).

Oxidant residual analysis was performed twice on each dechlorinated and chlorinated sample. Only one analysis was performed on the unchlorinated sample to check for background oxidant residual. During the sampling period two separate analyses of oxidant residual were performed on both dechlorinated and chlorinated samples. The average of the two analyses are reported in the results. During each analysis period (twice per sampling period) both TOR's and FOR's were measured. One measurement immediately following the other. However, an error is inherent in this procedure due to residual oxidant decay. For example, if TOR is performed before FOR, a time lapse of approximately 2.0 minutes occurs before the second analysis (FOR) can be completed. Therefore, the FOR measurement is not strictly comparable with the TOR measurement because during the 2 minutes the FOR level has decreased due to oxidant residual decay. To facilitate a valid comparison of TOR with FOR the value of the second parameter measured requires adjustment to the same analysis time frame as the first parameter. In the above example, measured FOR values require time frame adjustment to compensate for decay and allow a valid comparison with TOR measurements.

## FOR and TOR Time Frame Adjustments

A procedure for measuring TOR and FOR for adjustment of values between the second and the first analysis time frame results was developed. This procedure consisted of two similar measurement techniques identified as "A" and "B". Technique "A" is the measurement of TOR, followed immediately by FOR measurement, followed immediately by another TOR measurement for a single sample. Technique "B" differs from "A" by the order of measurement, first measurement of FOR, followed immediately by a TOR measurement, followed immediately by another FOR measurement. Differences of the first and third measurements (technique "A" difference of TOR's, technique "B" difference of FOR's) were computed and averaged for a few sets of samples. One-half of the average value of the first and third analysis results is used to adjust second analysis results to the first analysis time frame. For example, one-half of the average difference of the first and third measurements (TOR's) of all the samples measured in technique "A" was added to TOR values for those analyses periods where FOR was measured first and TOR measurement second (technique "B"). Similarly, for analysis periods when TOR was measured first and FOR second, an average computed rate of decay value is added to the FOR value to obtain an adjusted value. This method of adjustment was used on those values noted in the results and has two main disadvantages that should be noted. The method assumes a linear decay rate of the residual oxidants because of a lack of available data pertaining to decay rates at the low levels of residual oxidant encountered in chlorinated sea water. However, due to the short duration of the analysis period (less than 5 minutes) for completion of all three analyses (as described by techniques "A" and "B"), linearity appears to be a valid assumption. The other disadvantage is the adjustment creates a larger uncertainty in the calculated values than for a measured oxidant residual value. However, this time adjustment of measured values is required to facilitate a valid comparison of results.

Based on the measurement accuracy of  $\pm 0.01$  ppm and the computed standard deviation of 0.01 ppm for the sets of results used to adjust FOR and TOR values, the accuracy of the adjusted FOR's and TOR's is  $\pm 0.03$  ppm. The accuracy of COR's is  $\pm 0.04$  ppm.

### Dissolved Oxygen, pH and Temperature

Dissolved oxygen, pH and temperature were measured at the end of the sampling period for all samples. The dissolved oxygen was measured using a portable Chemtrix oxygen meter (model 5946-10) with an accuracy of  $\pm 0.2$  ppm (3). pH was measured with an Analytical Measurements Inc., portable pH meter (model No. 107). Temperature was measured with a mercury thermometer.

### LABORATORY ANALYSIS

Two samples of the cooling water from each sampling location were collected for laboratory analysis. The samples, one preserved with sulfuric acid and the other unpreserved, were stored in an ice chest for daily pickup and subsequent analysis. Table 1 presents the constituents measured and analytical methods used, including accuracies and detection limits of each method.

TABLE 1. CONSTITUENTS MEASURED AND ANALYTICAL METHODS, ACCURACIES AND DETECTION LIMITS

Constituent Measured	Analytical Method	Measurement Accuracy(8)*	Detection Limit (8)
Organic Nitrogen (as N)	Kjeldahl digestion	0.01	$\pm 0.03$
Ammonia Nitrogen (as N)	Distillation and Nesslerization	0.05	$\pm 0.03$
Total Organic Carbon	Infrared Analyzer	1	$\pm 1$
Biochemical Oxygen Demand	Incubation followed by dissolved oxygen determination	3	$\pm 1$
Bromide	Specific ion electrode	0.1	**
Chloride	Specific ion electrode	1	**

\* 95% Confidence Limit

\*\* Insufficient data were generated to statistically calculate a meaningful standard deviation. However precision was determined to be  $\pm 1.5\%$  for duplication of chlorides with a 101% recovery of spike and  $\pm 8\%$  for duplication of bromide with a 91% recovery of spike.



## SECTION 6

### ANALYTICAL RESULTS AND ASSOCIATED PLANT OPERATING PARAMETERS

Data collected and analytical results relating to each of the 28 tests are presented and discussed in this section.

#### DATA COLLECTED

During each field test the plant operating data presented in Table 2 were recorded. The reported chlorine and sulfur dioxide feed rates are of limited accuracy due to difficulties in reading the gas flow meters. This difficulty resulted from erratic fluctuation of the flowmeter float. Cooling water flow rates reported were based on the original design flow rate for the circulating water pumps and are also of limited accuracy. Sampling dates, times and tide conditions are also shown in Table 2. These uncertainties affect the chlorine dosage calculated and presented in Table 3 also.

#### ANALYTICAL RESULTS

The results of the field testing and the associated laboratory analytical results are presented in Tables 3, 4, 5 and 6.

Oxidant residuals measured at the chlorinated condenser outlet ranged from 0.122 to 0.339 mg/l TOR, 0.062 to 0.273 mg/l FOR and 0.012 to 0.135 mg/l COR\*. Oxidant residuals of dechlorinated effluent and unchlorinated condenser outlet samples were below the detection limit of 0.03 mg/l. Therefore, results for FOR and COR are not presented.

pH varied from 7.0 to 7.7 with no significant trends for the chlorinated condenser outlet, dechlorinated and unchlorinated condenser outlet samples. Dissolved oxygen varied from 3.4 to 7.0 mg/l without any distinguishable trends between the three sampling locations.

\* Tests 1-3 not included because of different sampling and analysis procedure as discussed in Section 4.0.

TABLE 2. SELECTED SAMPLING TIDES AND CORRESPONDING PLANT  
OPERATING PARAMETERS

Test No.	Date	Time	Tide Condition	Load MW	Cooling Water Flowrate (m <sup>3</sup> /sec)		Condensor Inlet °C	Temperature Outlet °C	Chlorine Feed Rate (Kg/hr)	Sulfur Dioxide Feed Rate (Kg/hr)
					Tunnel #1	Tunnel #2				
1	9/5	0900	Flood	173	3.1	2.8	17	28	9.5	9.0
2	9/5	1500	Ebb	133	3.1	2.8	16	25	9.1	7.9
3	9/6	0900	Flood	173	3.1	2.8	16	27	9.5	7.7
4	9/6	1500	Ebb	174	3.1	2.8	16	25	9.3	7.7
5	9/7	1500	Ebb	173	3.1	2.8	16	26	8.0	7.7
6	9/11	0900	Ebb	53	3.1	2.8	16	21	9.3	7.4
7	9/11	1530	Flood	60	3.1	2.8	16	26	9.0	7.7
8	9/12	0900	Ebb	143	3.1	2.8	17	27	9.0	7.9
9	9/12	1500	Flood	140	3.1	2.8	17	27	8.9	7.4
10	9/13	0900	Ebb	175	3.1	2.8	18	29	8.9	7.9
11	9/13	1500	Flood	180	3.1	2.8	17	29	8.9	7.7
12	9/14	0900	Ebb	178	3.1	2.8	17	30	9.0	8.9
13	9/14	1500	Flood	180	3.1	2.8	18	27	9.7	7.1
14	9/15	0900	Flood	180	3.1	2.8	18	27	9.7	7.7
15	9/15	1500	Ebb	180	3.1	2.8	18	27	9.7	6.8
16	9/16	0900	Flood	180	3.1	2.8	18	27	9.7	7.7
17	9/16	1500	Ebb	180	3.1	2.8	18	27	9.8	6.8
18	9/17	0900	Flood	180	3.1	2.8	17	27	10.0	7.6
19	9/17	1500	Ebb	180	3.1	2.8	17	27	9.8	7.1
20	9/18	0900	Flood	180	3.1	2.8	17	27	9.5	7.6
21	9/18	1500	Ebb	180	3.1	2.8	18	27	9.5	7.6
22	9/19	0900	Flood	180	3.1	2.8	18	26	9.1	7.2
23	9/19	1500	Ebb	180	3.1	2.8	17	26	9.5	7.6
24	9/20	0900	Flood	180	3.1	2.8	16	26	4.7	7.6
25	9/20	1500	Ebb	180	3.1	2.8	16	26	9.5	7.1
26	9/21	0900	Flood	180	3.1	2.8	17	27	9.0	7.1
27	9/21	1500	Ebb	180	3.1	2.8	17	27	9.0	6.9
28	9/22	0900	Flood	180	3.1	2.8	17	27	9.3	6.6

TABLE 3. CHLORINATED CONDENSER OUTLET FIELD DATA

Test No.	Chlorine Dose * (mg/l)	TOR (mg/l)	FOR (mg/l)	COR** (mg/l)	pH	D.O. (mg/l)	Temperature (°C)
1	0.85	0.052	<0.03	0.052	7.4	3.9	27.0
2	0.82	0.027	<0.03	0.027	7.5	3.7	27.0
3	0.85	0.093	0.053	0.040	7.4	4.9	28.0
4	0.83	0.200	0.118	0.082	7.1	4.7	28.0
5	0.72	0.269	0.221	0.077	7.4	5.4	28.0
6	0.83	0.178	0.164	0.012	7.3	5.0	24.0
7	0.81	0.122	0.062	0.091	7.4	5.8	25.0
8	0.81	0.168	0.106	0.135	7.4	5.5	27.0
9	0.80	0.213	0.126	0.087	7.4	5.4	29.5
10	0.80	0.217	0.152	0.065	7.4	5.4	28.0
11	0.80	0.206	0.146	0.060	7.3	5.4	28.5
12	0.81	0.225	0.158	0.067	7.6	7.0	28.0
13	0.87	0.243	0.176	0.067	7.3	5.4	28.0
14	0.87	0.265	0.222	0.043	7.6	5.5	27.0
15	0.87	0.315	0.232	0.083	7.5	5.1	27.0
16	0.87	0.281	0.194	0.087	7.6	5.2	28.0
17	0.88	0.320	0.234	0.086	7.6	4.8	28.0
18	0.89	0.339	0.267	0.072	7.4	5.1	28.0
19	0.88	0.331	0.263	0.064	7.0	5.0	27.0
20	0.85	0.277	0.246	0.031	7.6	5.3	27.0
21	0.85	0.289	0.212	0.077	7.6	5.4	27.0
22	0.82	0.259	0.205	0.054	7.5	5.0	27.5
23	0.85	0.304	0.241	0.063	7.6	5.0	26.0
24	0.42	0.140	0.104	0.036	7.7	5.3	26.0
25	0.85	0.306	0.259	0.047	7.7	5.4	26.0
26	0.81	0.270	0.227	0.043	7.7	5.0	27.0
27	0.81	0.256	0.233	0.023	7.7	5.4	27.0
28	0.83	0.322	0.273	0.049	7.7	5.2	27.8

\* Calculated based on chlorine and cooling water flow rates

\*\* Calculated: TOR - FOR = COR

TABLE 4. DECHLORINATED EFFLUENT FIELD DATA

Test No.	TOR (mg/l)	pH	D.O. (mg/l)	Temperature (°C)
1	<0.03	7.4	3.7	27.0
2	<0.03	7.6	3.9	27.0
3	<0.03	7.4	4.7	28.0
4	<0.03	7.4	5.8	28.0
5	<0.03	7.4	5.2	27.0
6	<0.03	7.3	4.8	24.0
7	<0.03	7.4	5.3	25.0
8	<0.03	7.4	5.5	27.0
9	<0.03	7.4	5.1	28.5
10	<0.03	7.4	5.4	27.0
11	<0.03	7.4	5.0	28.0
12	<0.03	7.4	5.4	27.5
13	<0.03	7.3	5.5	27.5
14	<0.03	7.4	4.9	27.0
15	<0.03	7.5	5.1	27.0
16	<0.03	7.6	5.1	28.5
17	<0.03	7.6	5.4	28.5
18	<0.03	7.4	5.5	27.0
19	<0.03	7.7	5.4	27.0
20	<0.03	7.7	5.6	27.0
21	<0.03	7.6	5.5	27.0
22	<0.03	7.4	5.2	27.0
23	<0.03	7.7	5.4	26.0
24	<0.03	7.6	5.4	26.0
25	<0.03	7.7	5.6	26.0
26	<0.03	7.6	5.4	26.0
27	<0.03	7.7	4.9	27.0
28	<0.03	7.7	5.6	27.8

TABLE 5. UNCHLORINATED CONDENSER OUTLET FIELD DATA

Test No.	TOR (mg/l)	pH	D.O. (mg/l)	Temperature (°C)
1	<0.03	7.6	3.5	26.0
2	<0.03	7.3	3.4	27.0
3	<0.03	7.5	5.2	28.0
4	<0.03	7.4	5.4	28.0
5	<0.03	7.2	5.5	27.0
6	<0.03	7.4	5.6	24.0
7	<0.03	7.4	5.3	25.0
8	<0.03	7.4	5.9	27.0
9	<0.03	7.4	5.9	29.5
10	<0.03	7.4	5.7	28.0
11	<0.03	7.4	6.0	28.5
12	<0.03	7.0	5.8	28.0
13	<0.03	7.4	5.8	28.0
14	<0.03	7.5	5.4	27.0
15	<0.03	7.5	5.4	27.0
16	<0.03	7.7	5.3	28.0
17	<0.03	7.7	5.7	28.0
18	<0.03	7.4	5.5	28.0
19	<0.03	7.7	5.5	27.0
20	<0.03	7.7	5.5	27.0
21	<0.03	7.6	5.8	27.0
22	<0.03	7.6	5.4	27.0
23	<0.03	7.7	5.7	27.0
24	<0.03	7.7	5.5	26.0
25	<0.03	7.7	5.6	26.0
26	<0.03	7.6	5.4	27.0
27	<0.03	7.7	5.8	27.0
28	<0.03	7.7	5.8	27.8

TABLE 6. LABORATORY ANALYTICAL DATA

Test No.	BOD mg/ℓ			C	TOC mg/ℓ			Ammonia Nitrogen mg/ℓ			Organic Nitrogen mg/ℓ			Bromide mg/ℓ			Chloride mg/ℓ		
	C*	DC+	RW†		DC	RW	C	DC	RW	C	DC	RW	C	DC	RW	C	DC	RW	
1	2	2	2	3	<3	<3	0.28	0.06	0.13	0.54	0.35	0.25	86	87	84	17510	17360	17360	
2	2	1	2	<3	<3	<3	0.08	0.11	0.11	0.29	0.25	0.30	50	50	50	17210	17210	17310	
3	1	1	1	<3	<3	<3	0.12	0.13	0.14	0.28	0.34	0.48	81	61	59	17310	17260	17310	
4	<1	1	1	<3	<3	<3	0.06	0.07	0.08	0.25	0.30	0.31	71	73	71	17560	17560	17410	
5	<1	1	1	<3	<3	<3	0.07	0.10	0.09	0.26	0.24	0.23	79	77	70	17560	17610	17660	
6	1	1	2	<3	<3	<3	0.08	0.10	0.11	0.48	0.19	0.33	59	77	71	17360	17210	17460	
7	1	2	1	<3	<3	<3	0.08	0.09	0.09	0.32	0.32	0.40	64	64	56	17360	17610	17410	
8	1	1	3	<3	<3	<3	0.09	0.09	0.09	0.37	0.30	0.26	73	81	64	17510	17310	17610	
9	1	2	1	<3	<3	<3	0.08	0.10	0.09	0.34	0.32	0.30	73	74	77	17460	17360	17410	
10	2	1	1	<3	<3	<3	0.21	0.15	0.14	0.26	0.27	0.08	73	70	67	17410	17260	17360	
11	1	1	2	<3	<3	<3	0.09	0.09	0.10	0.36	0.27	0.36	49	49	49	17260	17310	17210	
12	1	1	1	<3	<3	<3	0.08	0.07	0.08	0.34	0.32	0.30	62	61	76	17210	17210	17310	
13	2	1	1	<3	<3	<3	0.10	0.10	0.09	0.58	0.29	0.37	62	60	49	17310	17310	17210	
14	1	2	1	<3	<3	<3	0.07	0.09	0.07	0.29	0.29	0.30	68	65	67	17560	17410	17460	
15	1	2	1	<3	<3	<3	0.06	0.07	0.07	0.37	0.31	0.35	64	65	65	17360	17310	17510	
16	1	2	1	<3	<3	<3	0.07	0.06	0.08	0.27	0.25	0.24	73	68	64	17310	17410	17310	
17	1	1	2	<3	<3	<3	0.08	0.07	0.08	0.24	0.10	0.22	66	69	75	17510	17410	17610	
18	1	1	1	<3	<3	<3	0.06	0.07	0.11	0.25	0.30	0.28	62	61	76	17260	17460	17460	
19	1	1	1	<3	<3	<3	0.08	0.08	0.09	0.33	0.37	0.32	63	63	64	17210	17260	17310	
20	1	<1	1	<3	<3	<3	0.07	0.08	0.08	0.35	0.36	0.32	65	65	52	17260	17310	17310	
21	1	1	1	3	3	3	0.11	0.09	0.09	0.30	0.27	0.24	63	60	65	17410	17460	17410	
22	1	1	1	4	4	3	0.07	0.08	0.09	0.41	0.57	0.34	54	60	72	17360	17360	17110	
23	1	2	1	<3	<3	<3	0.06	0.07	0.07	0.39	0.34	0.34	57	57	60	17310	17310	17460	
24	1	1	2	<3	<3	<3	0.09	0.08	0.08	0.33	0.30	0.31	90	88	65	17310	17460	17460	
25	1	1	1	<3	<3	<3	0.05	0.05	0.06	0.35	0.32	0.31	63	63	67	17310	17610	17710	
26	1	1	1	<3	<3	<3	0.07	0.08	0.08	0.31	0.34	0.27	88	88	77	17360	17360	17410	
27	1	2	1	3	3	3	0.08	0.07	0.08	0.32	0.29	0.29	53	--**	68	17460	17360	17460	
28	1	2	1	3	<3	3	0.06	0.13	0.07	0.34	0.25	0.29	86	82	35	17610	17510	17510	

\* C - Chlorinated condensor outlet

+ DC - Dechlorinated effluent

† RW - Unchlorinated condensor outlet

\*\* - Unreliable results obtained

BOD and TOC values were very low and there are no apparent trends for results obtained from the three sampling locations. BOD values were generally 1-2 mg/l. A majority of the TOC values were below detection level. A few TOC values of 3 and 4 mg/l (near the detection limit) were reported.

Organic nitrogen values were generally about three times the ammonia nitrogen values. Organic nitrogen values varied from 0.10 to 0.54 mg/l. Ammonia nitrogen values varied from 0.04 to 0.28 mg/l. There does not appear to be any correlations between results for the three sampling locations.

### Discussion of Results

PG&E's Potrero power plant dechlorination system was shown to operate effectively for removal of oxidant residual from the cooling water system based on results obtained by this program. As shown in Table 4, TOR values were less than the 0.03 mg/l detection limit of the amperometric titrator for the 28 sampling periods. It should be noted that the unchlorinated and chlorinated streams are combined before dechlorination occurs. Therefore, the chlorinated stream is diluted by the unchlorinated stream, effectively halving TOR levels reported for the chlorinated stream. For example consider test number 18, TOR was 0.339 mg/l (highest value reported during the 28 sampling periods) in the chlorinated stream. However, due to the dilution discussed above, the dechlorinator treated a combined stream with a TOR concentration of only 0.18 mg/l.

Examination of the residual oxidant measurements with respect to tidal conditions show no apparent correlation. However, due to the very slight variations in cooling water characteristics, as indicated by the parameters measured, a correlation between tidal conditions and residual oxidant levels would not be expected.

It was not possible to determine the effects of organic loading on dechlorination operation due to the very low organic loading of the cooling water as indicated by the BOD and TOC values reported in Table 6.

## SECTION 7

### LABORATORY EVALUATION OF TEMPERATURE EFFECT ON DECHLORINATION EFFICIENCY

The objective of this task was to evaluate the effect of different temperatures on the efficiency of dechlorination at conditions similar to those existing at the Potrero power plant based on results obtained from a laboratory jar test. During this evaluation chlorination levels, and dechlorination reaction times selected were those prevailing at the Potrero power plant. Also local bay water, collected near the cooling water intake, was used.

The evaluation procedure consisted of chlorination and dechlorination at different temperatures ranging from 14°C to 35°C (60° to 95°F). During the determination, power plant chlorination/dechlorination practices were incorporated where viable. Total oxidant residuals were measured after chlorination and after dechlorination by amperometric titration.

The following procedure was employed on several different samples at various temperatures. One liter samples of sea water were chlorinated with sodium hypochloride to attain oxidant levels of approximately 1.0 ppm. Samples were analyzed for TOR, pH and D.O. after a period of time to allow for reaction and stabilization. Following TOR measurement each sample was dechlorinated with sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ). A sufficient quantity of sodium thiosulfate was added to the sample to react with part of the oxidants present while leaving a measurable oxidant residual. This residual oxidant was required to calculate removal efficiencies. Immediately after dechlorination TOR was measured again.

Values of TOR after chlorination and after dechlorination, along with removal efficiencies are presented in Table 7. Dissolved oxygen and pH were measured at 5.6 ppm and 7.4, respectively, without a significant deviation throughout the experiment.



TABLE 7. TEMPERATURE EFFECT VS DECHLORINATION EFFICIENCY

Temp (°C)	TOR after Cl <sub>2</sub> *	TOR after DCl <sub>2</sub> **	% TOR Removal
14	1.154	0.644	44.2
18	1.384	0.778	43.8
21	1.411	0.829	41.2
25	1.314	0.659	49.8
25	1.230	0.661	46.3
34	1.214	0.632	47.9
36	1.192	0.514	56.8

\* Cl<sub>2</sub> - Chlorination

\*\* DCl<sub>2</sub> - Dechlorination

Removal efficiencies for TOR shown in Table 7 show a slight increasing trend with higher temperatures. During laboratory testing it was observed that as the temperature of the samples increased, the TOR remaining in the samples after chlorination decreased, even though chlorine dosage was constant. Since equal quantities of dechlorination compound were added to each sample, the increase in TOR removal efficiency is partially due to the decrease in TOR before dechlorination as temperature increases. It can not be concluded that the increase in TOR removal efficiency is entirely associated with temperature effects on the dechlorination reaction.

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## APPENDIX A

### EVALUATION OF THE EFFECT OF SAMPLE COLLECTION ON VOLATILE ORGANIC COMPOUNDS

In order to determine if volatile organic compound measurements would be significantly affected by collection with the designed field sampling system (see Section 3.0 for details of the sampling system), the following experiment was performed.

Solutions of haloforms, particularly chloroform, bromoform, bromodichloromethane and chlorodibromomethane, at concentrations of 30 ppb, 10 ppb and 1 ppb, were prepared. Each solution was induced into the sampling system with the vacuum pump used for field sampling. Samples of each solution (before and after collection by sampling system) were analyzed by West Coast Technical Service, Inc. using a gas chromatograph-mass spectrometer. Table A-1 shows haloform concentrations before and after collection. Samples labeled 30B, 10B and 1B represent samples after vacuum collection. The other three samples are before vacuum collection. As shown in the table, no significant changes in organic concentrations were noticed.

TABLE A-1. VOLATILE ORGANIC LOSSES

<u>Sample</u>	<u>Micrograms/Liter</u>			
	<u>Chloroform</u>	<u>Bromoform</u>	<u>Bromodichloro- methane</u>	<u>Chlorodibromo- methane</u>
30B	30	28	29	30
10B	10	10	9	12
1B	4	TR<5	3	2
30 PPB Haloforms	33	31	30	25
10 PPB Haloforms	11	9	10	10
1 PPB Haloforms	1	ND<5	1	ND<1

TR = Trace amount detected

ND = Not detected

## APPENDIX B

### SELECTION OF EBB AND FLOOD TIDE SAMPLING CONDITIONS

One of the objectives of this program was to evaluate dechlorination during the two different tide conditions, ebb and flood. 14 sampling periods of each ebb and flood tide conditions were selected using the tide table (Table B-1). Tides were selected to correspond with the chlorination/dechlorination cycle at the power plant. Tide conditions were selected for 0900 and 1500 chlorination cycles with careful attention that tide conditions did not change during a sampling period.

Low and high tides indicated in Table B-1 are referenced to the Golden Gate bridge. Times were corrected for the difference in tide times at the Potrero power plant. Based on information from plant personnel and visual observation an adjustment of approximately 30 additional minutes to the times in Table B-1 was deemed necessary. Table B-2 presents the date, time and tide for each of the samples collected.

TABLE B-1. TIDES AT SAN FRANCISCO (Golden Gate), CALIFORNIA - 1979

Pacific Daylight Saving Time

(Heights in feet)

SEPTEMBER		Time and Height of High and Low Water							
Day		Time	Ht.	Time	Ht.	Time	Ht.	Time	Ht.
Sat.	1	0134	0.5	0857	4.2	1329	2.9	1941	5.9
Sun.	2	0231	0.1	0952	4.6	1431	2.6	2044	6.1
Mon.	3	0324	-0.4	1038	4.9	1526	2.2	2140	6.3
Tue.	4	0411	-0.7	1117	5.2	1617	1.8	2235	6.5
Wed.	5	0457	-0.8	1156	5.4	1707	1.3	2330	6.5
Thu.	6	0539	-0.7	1234	5.7	1756	0.9	--	--
		Hi Water		Lo Water		Hi Water		Lo Water	
Fri.	7	0023	6.3	0625	0.5	1313	5.9	1845	0.5
Sat.	8	0118	6.0	0707	0.0	1355	6.0	1939	0.4
Sun.	9	0214	5.6	0753	0.6	1437	6.0	2034	0.3
Mon.	10	0314	5.1	0841	1.3	1521	6.0	2131	0.4
Tue.	11	0423	4.7	0933	1.9	1610	5.9	2239	0.5
Wed.	12	0540	4.4	1039	2.4	1706	5.7	2350	0.6
Thu.	13	0705	4.4	1155	2.7	1807	5.6	--	--
		Lo Water		Hi Water		Lo Water		Hi water	
Fri.	14	0059	0.6	0825	4.5	1311	2.8	1909	5.5
Sat.	15	0203	0.6	0918	4.7	1417	2.7	2012	5.5
Sun.	16	0257	0.5	1008	4.9	1509	2.4	2108	5.5
Mon.	17	0341	0.4	1045	5.0	1555	2.1	2159	5.5
Tue.	18	0419	0.4	1119	5.0	1634	1.8	2242	5.4
Wed.	19	0454	0.4	1146	5.1	1709	1.6	2321	5.3
Thu.	20	0526	0.5	1213	5.1	1745	1.3	2359	5.2
Fri.	21	0555	0.7	1238	5.1	1817	1.1	--	--
		Hi Water		Lo Water		Hi Water		Lo Water	
Sat.	22	0038	5.1	0626	0.9	1304	5.2	1849	1.0

TABLE B-2. SELECTED SAMPLING TIDES

Sample No.	Date	Time	Tide
1	9/5	0900	Flood
2	9/5	1500	Ebb
3	9/6	0900	Flood
4	9/6	1500	Ebb
5	9/7	1500	Ebb
6	9/11	0900	Ebb
7	9/11	1530	Flood
8	9/12	0900	Ebb
9	9/12	1500	Flood
10	9/13	0900	Ebb
11	9/13	1500	Flood
12	9/14	0900	Ebb
13	9/14	1500	Flood
14	9/15	0900	Flood
15	9/15	1500	Ebb
16	9/16	0900	Flood
17	9/16	1500	Ebb
18	9/17	0900	Flood
19	9/17	1500	Ebb
20	9/18	0900	Flood
21	9/18	1500	Ebb
22	9/19	0900	Flood
23	9/19	1500	Ebb
24	9/20	0900	Flood
25	9/20	1500	Ebb
26	9/21	0900	Flood
27	9/21	1500	Ebb
28	9/22	0900	Flood

<b>TECHNICAL REPORT DATA</b> <i>(Please read Instructions on the reverse before completing)</i>		
1. REPORT NO. <b>EPA-600/7-80-049</b>	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE <b>Residual Oxidants Removal from Coastal Power Plant Cooling System Discharges: Field Evaluation of SO2 Addition System</b>		5. REPORT DATE <b>March 1980</b>
7. AUTHOR(S) <b>K. Scheyer and G. Houser</b>		6. PERFORMING ORGANIZATION CODE
9. PERFORMING ORGANIZATION NAME AND ADDRESS <b>TRW, Inc. One Space Park Redondo Beach, California 90278</b>		8. PERFORMING ORGANIZATION REPORT NO.
12. SPONSORING AGENCY NAME AND ADDRESS <b>EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711</b>		10. PROGRAM ELEMENT NO. <b>INE624A</b>
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15. SUPPLEMENTARY NOTES <b>IERL-RTP project officer is Julian W. Jones, Mail Drop 61, 919/541-2489.</b>		
16. ABSTRACT <p>The report gives results of an evaluation of the performance of a dechlorination system that uses SO<sub>2</sub> to remove residual oxidants from chlorinated sea water in a power plant cooling system. Samples of unchlorinated, chlorinated, and dechlorinated cooling water were obtained at Pacific Gas and Electric's Potrero power plant in San Francisco. The samples were collected during 28 sampling periods--14 at flood tide and 14 at ebb tide--and analyzed for several chemical and physical constituents. An amperometric titrator was used for field analysis of total oxidant residual (TOR) and free oxidant residual (FOR). Analytical results, plant operating data, and laboratory experiments were used to evaluate the dechlorination system. Major conclusions include: (1) the dechlorination system studied showed effective removal of residual oxidants from chlorinated sea water used in the power plant cooling system; (2) the dechlorination system proved reliable (no measurable oxidant residual was found at the effluent outfall); and (3) due to the effectiveness of the dechlorination system in removing all measurable oxidant residual, average and maximum levels of dechlorination cannot be determined.</p>		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
<b>Pollution                      Oxidizers</b> <b>Dechlorination</b> <b>Cooling Systems</b> <b>Sea Water</b> <b>Electric Power Plants</b> <b>Sulfur Dioxide</b>	<b>Pollution Control</b> <b>Stationary Sources</b> <b>Oxidant Removal</b>	<b>13B                      11G</b> <b>07A, 07B, 07C</b> <b>13A</b> <b>08J</b> <b>10B</b>
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