

PILGRIM NUCLEAR POWER STATION

Procedure No. 7.2.40

INTAKE CANAL, DISCHARGE CANAL, AND SCREENWASH SAMPLING AND TRC ANALYSIS



Stop
Think
Act
Review

INFORMATIONAL USE

MSTP RELATED

REVISION LOG

REVISION	10	Date Originated	7/04
<u>Pages Affected</u>		<u>Description</u>	
11		Add step to close out applicable MSTP Rep Task.	
11		Add step to obtain Supervisor review.	
14,17		Add Chemistry Supervisor signoff.	
REVISION	9	Date Originated	7/03
<u>Pages Affected</u>		<u>Description</u>	
9		Clarify Note to allow flexibility in discharge canal TRC sample times.	
11,14		Clarify temperature measurement as °F.	
REVISION	8	Date Originated	6/03
<u>Pages Affected</u>		<u>Description</u>	
14		Add Screenwash TRC to Total Residual Chlorine in Discharge Canal (Attachment 1).	
19		Add reference to Attachment 1.	

TABLE OF CONTENTS

	<u>Page</u>
1.0 PURPOSE AND SCOPE.....	4
2.0 REFERENCES.....	4
3.0 DEFINITIONS.....	5
4.0 DISCUSSION.....	5
5.0 SPECIAL TOOLS AND EQUIPMENT.....	5
6.0 PRECAUTIONS AND LIMITATIONS.....	6
7.0 PREREQUISITES.....	7
8.0 PROCEDURE.....	8
8.1 PRELIMINARY SETUP FOR HYPO INJECTION.....	8
8.2 DETERMINATION OF TOTAL RESIDUAL CHLORINE.....	9
8.3 WEEKLY pH SAMPLING AND SCREENWASH TRC.....	11
8.4 THERMAL BACKWASH SAMPLING.....	12
9.0 ACCEPTANCE CRITERIA.....	13
10.0 ATTACHMENTS.....	13
ATTACHMENT 1 - FORM CH-43, TOTAL RESIDUAL CHLORINE IN DISCHARGE CANAL....	14
ATTACHMENT 2 - WEEKLY CHLORINE STANDARD CHECK.....	16
ATTACHMENT 3 - SAMPLE DURING THERMAL BACKWASH.....	17
ATTACHMENT 4 - DETERMINATION OF SCREENWASH TOTAL RESIDUAL CHLORINE.....	18

1.0 PURPOSE AND SCOPE

This Procedure provides direction for the sampling and analysis of discharge canal water and screenwash for total residual chlorine (TRC) concentration.

Also included are sampling and analysis of seawater from the intake, discharge, and screenwash system to monitor pH and temperature which are also governed by the NPDES permit.

2.0 REFERENCES

2.1 DEVELOPMENTAL

- [1] 40CFR136, Guidelines Establishing Test Procedures for the Analysis of Pollutants
- [2] FSAR Section 11.6.3
- [3] National Pollutant Discharge Elimination System (NPDES) Permit (No. MA0003557 Federal, No. 359 State)
- [4] PDC90-42
- [5] PNPS SI-CH.3310, *"Total Residual Chlorine Analysis In Discharge Canal"* (retired)

2.2 IMPLEMENTING

- [1] ENN-LI-102, *"Corrective Action Process"*
- [2] Instruction Book - Wallace & Tiernan Amperometric Titrator (Series A-790)"
- [3] Procedures
 - (a) PNPS 2.2.95, *"Chlorination System"*
 - (b) PNPS 7.1.77, *"Shelf Life of Chemicals"*
 - (c) PNPS 7.2.33, *"pH Measurement"*
 - (d) PNPS 7.8.1, *"Water Quality Limits"*
- [4] Standard Methods for the Examination of Water and Waste Water, 20th Edition, Method No. 4500-C1 E, *"Amperometric Titration Method"*

3.0 DEFINITIONS

- [1] Chlorination or hypochlorination - Injection of liquid sodium hypochlorite solution (10% NaOCl) into raw cooling water (seawater) to prevent or control marine biofouling (slime growth, mussels, etc.).
- [2] Duplicate Sample - A separate sample taken at the same time and from the same process stream as an original sample. It is usually analyzed by the same technician using the same method at the same time as the original sample.
- [3] Total Residual Chlorine (TRC) - The concentration of all oxidants in a solution of chlorinated seawater which, at pH 4, cause added iodide to be converted to iodine. Amperometric titration with phenylarsine oxide is the analytical method approved by US EPA, with the results expressed as "ppm TRC", equivalent to "mg/L Total Residual Oxidants" (TRO).

4.0 DISCUSSION

NPDES Permit limits the concentration of total residual chlorine discharged to Cape Cod Bay. It is imperative that during Condenser (or CWS) chlorination samples be collected and analyzed for the entire period of hypochlorination. Concurrent with the responsibility of such sampling and analysis is the necessity of accurate recordkeeping. In essence, the Procedure consists of having the necessary analytical equipment and chemicals set up before the injection of hypochlorite begins, collecting and analyzing samples of discharge canal water at prescribed intervals during and after the chlorination period, and finishing the analytical report for final signoff by the appropriate supervisor.

5.0 SPECIAL TOOLS AND EQUIPMENT

- [1] Amperometric titrator
- [2] pH 4 buffer solution
- [3] Phenylarsine oxide solution
- [4] Potassium iodide, 5% by weight (5 gm KI dissolved in 95 mL DI water, actual weights may be varied according to volume desired). Store in a dark container. Prepared solutions may also be purchased from the manufacturer.
- [5] Dilute hypochlorite solution (for titrator functional check)
- [6] Bucket and sufficient length of rope to drop the bucket from the pedestrian bridge into the canal (if sample pump is inoperative)
- [7] Fresh water (tap water or deionized water)

- [8] Orion Calibration Kit (purchased from vendor) containing:
- (a) Standard A or B (chlorine standards)
 - (b) Iodine standard
 - (c) Acid standard
- [9] For thermal backwash sampling: bucket and rope normally kept in oil lab inside door on floor. Used when pump is not operated.

6.0 PRECAUTIONS AND LIMITATIONS

- [1] Analysis for TRC must occur within 15 minutes of sampling or analysis is invalid.
- [2] Maintain the 200 mL or more water level in the titrator sample cup to prevent the saturated electrolyte from depleting and allowing the dry salt crystals to clog the cell and agitator.
- [3] Ensure the cell plug is in place in the cell and electrolyte tablets are present. Replace in accordance with Instruction Book - Wallace & Tiernan Amperometric Titrator (Series A-790), if required.
- [4] Unplug the titrator prior to servicing.
- [5] Phenylarsine oxide is a toxic chemical.
- [6] Potassium iodide is a photo-sensitive chemical. Consult PNPS 7.1.77 for shelf life.
- [7] The maximum instantaneous concentration for discharge canal total residual chlorine is listed in PNPS 7.8.1 as the Control Limit. If this limit is exceeded, immediately contact the Operator to secure hypochlorite injection, then notify Chemistry Supervision. Chemistry Supervision is to notify the PNPS Senior Marine Fisheries Biologist in Regulatory and Industry Affairs and initiate a Condition Report (CR).

The TRC target concentration is 0.06 ppm (mg/L). However, PNPS 7.8.1 provides Achievable Limits that the TRC concentration should be within.

Once hypochlorination is underway, the injection rate may be increased in gradual steps provided that a waiting period of at least 20 minutes shall be observed prior to an increase in the hypo injection rate (when two CW pumps are operating). If only one CW pump is in service, then a waiting period of at least 40 minutes applies prior to increasing the hypo injection rate.

- [8] When only one CW pump is in operation, there is an increased risk of overchlorination. Do not perform hypochlorination with only one CW pump running unless:
- (a) Permission is obtained from both the SM and the Chemistry Superintendent.
 - (b) Sea conditions near the mouth of the discharge canal are less than 2 feet (no storm surges).
- [9] If the amperometric titrator is deemed inoperative, chlorination shall not be started; or if in progress and the titrator fails, hypochlorite injection shall be shut down.
- [10] Amperometric titrator is not calibrated on the $\mu\text{g/L}$ scale.

7.0 PREREQUISITES

None

8.0 PROCEDURE

NOTES

1. A reliable means of two-way communication between the Chemistry Technician and the Operator must be in place prior to, and maintained during, hypochlorite injection. This may be accomplished using the plant paging system, radio, or other method previously approved by Chemistry Supervision.
2. The routine titrator functional check verifies that the instrument is operative. The 0.1 ppm chlorine standard check assures its accuracy.
3. Sections 8.1, 8.2, 8.3, and 8.4 may be performed in any order as deemed appropriate.

8.1 PRELIMINARY SETUP FOR HYPO INJECTION

- [1] **PROCEED TO** the room under the pedestrian footbridge **AND SET UP** apparatus.

NOTE

If the Chemistry Technician feels the need for a second safety person, one may be requested from the SM/CRS or Chemistry Supervisor.

- [2] **IF** sample pump is inoperative **AND** no replacement pump is immediately available, **THEN TAKE** samples from the discharge canal using a bucket and rope.
- [3] **COLLECT** a sample of ambient seawater **AND PLACE** it on the titrator.

NOTE

Titrator is not calibrated on the $\mu\text{g/L}$ scale.

- [4] **TURN** the rotary switch to the "mg/L" position. **ADJUST** the meter with the turns-counting dial so that the needle is in the lower half of the meter.
- [5] **ADD** 1 to 3 drops of dilute hypochlorite solution **AND OBSERVE** the reaction of the meter needle. **IF** the needle moves upward, titrator is operative; **PROCEED TO** Step 8.1[6]. **IF** the needle does NOT move or moves downward, the titrator is inoperative; **DO NOT** start the chlorination.

CAUTION

Phenylarsine oxide is a toxic chemical. Observe all precautions on label and wash hands thoroughly after handling.

- [6] **ENSURE** titrant reservoir (squeeze bottle) is filled with phenylarsine oxide solution (PAO).
- [7] **TURN** the rotary switch to the "STBY" position.
- [8] **RINSE** the cell and sample cup with fresh water or sample.
- [9] **WHEN** titrator operation has been deemed satisfactory, **NOTIFY** the Operator to begin injection **AND INDICATE** initial hypochlorite injection rate.
- [10] **WHEN** notified injection has begun, **RECORD** time injection started as well as which CW pump is being chlorinated by which hypo pump on Form CH-43 (Attachment 1).

NOTE

Grab samples should be collected every 10 to 20 minutes. Analysis shall occur within 15 minutes of sampling or sample is invalid.

- [11] **COLLECT** chlorination seawater samples at sample sink or from bucket **AND ANALYZE** in accordance with Section 8.2.
- [12] **COLLECT** a duplicate sample once during chlorination **AND ANALYZE** in accordance with Section 8.2.
- [13] **NOTE** the sample collection time on Form CH-43 **AND BEGIN** the analysis.

8.2 DETERMINATION OF TOTAL RESIDUAL CHLORINE

- [1] **FILL** pipet with titrant by squeezing titrant reservoir.
- [2] **RINSE** beaker with sample or fresh water.
- [3] **PLACE** 200 mL of sample in beaker **AND POSITION** beaker on titrator.

NOTE

Always add potassium iodide first and then pH 4 buffer (the dropper furnished with this unit delivers approximately 1 mL).

- [4] **TURN** rotary switch to the "mg/L" position.

- [5] **ADD** 1 mL of potassium iodide solution.
- [6] **ADD** 1 mL pH 4 buffer solution.
- [7] **IF** necessary, **ADJUST** meter with the turns-counting dial so the needle is near 100.
- [8] **NOTE** titrant level on the pipet (**ADJUST** as needed).
- [9] **ADD** PAO (phenylarsine oxide solution) from the pipet in small increments (0.01 or 0.02 mL) by turning the stopcock counterclockwise while watching needle on meter for downward deflection.
- [10] **IF** during the course of adding titrant the needle deflects below zero, **BRING** it back on scale by adjusting the turns-counting dial. End point is just passed when the addition of a small increment of titrant no longer deflects the needle to the left. **DO NOT** count this last amount in the volume titrated.
- [11] **WHEN** titration is finished, **ENTER** the volume titrated in the "Chlorine Conc. (ppm TRC)" column on Form CH-43 (Attachment 1).
- [12] **IF** after adding 0.05 mL of titrant there has been no significant needle deflection, **ENTER** 0.00 under "Chlorine Conc. (ppm TRC)".
- [13] **RECORD** TRC values with two decimal places (X.XX ppm). The amperometric titrator's limit of detection is approximately 0.02 ppm.
- [14] **IF** the instantaneous total residual chlorine limit of 0.1 ppm is exceeded, **IMMEDIATELY CONTACT** Operations to terminate hypochlorite injection **AND** **PERFORM** the following:
- (a) **CONTINUE** sampling until two confirming 0.00 ppm TRC results.
 - (b) **NOTIFY** Chemistry Supervisor as soon as possible after TRC reaches 0.00 ppm.
 - (c) Chemistry Supervisor shall notify the PNPS Senior Marine Fisheries Biologist in Regulatory and Industry Affairs.
 - (d) **SUBMIT** a CR.
- [15] **RECORD** corresponding data for "Hypo Pump Setting" and "Injection Rate" on Form CH-43. Between samples, **TURN** the rotary switch to the "STBY" position.
- [16] **WHEN** hypo injection is terminated, **RECORD** the time on Form CH-43.
- [17] **CONTINUE** sampling and analysis until two consecutive samples show 0.00 ppm after the addition of 0.05 mL of titrant. **RECORD** all on Form CH-43.

- [18] **DISPOSE** of sample. **RINSE** beaker and electrode with fresh water. **STORE** cell in fresh water.
- [19] **RECORD** duplicate sample result in Remarks/Comments column of Form CH-43.
- [20] **RECORD** the duplicate sample results in LABSTATS or equivalent. This step may be performed out of sequence.
- [21] **DETERMINE** the maximum and average ppm of total residual chlorine readings (**DO NOT** include measurements taken after injection has been stopped). **ENTER** on Form CH-43 **AND SIGN OFF** the form.

8.3 WEEKLY pH SAMPLING AND SCREENWASH TRC

- [1] **OBTAIN** a sample of the intake, discharge, and screenwash seawater **AND** a duplicate sample of one point.
 - (a) **RECORD** the pH (PNPS 7.2.33) and temperature (°F) of the samples on Attachment 1. (Preferably, these measurements will be taken using portable instrumentation when the samples are taken.)
 - (b) Another Chemistry Technician may be designated by Chemistry Supervision to obtain and analyze the screenwash sample.
 - (c) **RECORD** the duplicate sample results in LABSTATS or equivalent.
 - (d) **PERFORM** analysis of screenwash seawater TRC in accordance with Attachment 4.
- [2] **OBTAIN** supervisor review. |
- [3] **CLOSE** applicable MSTP Rep Task (S088038). |

8.4 THERMAL BACKWASH SAMPLING

NOTE

The purpose is to analyze thermal backwash discharge for pH and compare to a normal intake pH.

Either the thermal backwash or the intake sample may be sampled for the duplicate.

- [1] **OBTAIN** a sample of thermal backwash discharge by one of the following methods:
 - (a) **PUMP** a sample using the submersible pump during the thermal backwash of 'B' Bay.
 - **SWITCH** the pump power "ON".
 - **FLUSH** for at least 30 seconds.
 - **SAMPLE**.
 - **SWITCH** the pump power "OFF".
 - (b) **DIP SAMPLE** under the grating between the screens and trash rack.
 - (c) **DIP SAMPLE** at the walkway on the outer intake structure wall.
- [2] **ANALYZE** for pH in accordance with PNPS 7.2.33.
- [3] **SAMPLE AND ANALYZE** intake for pH prior to or after thermal backwash is complete.
- [4] **RECORD** results on Attachment 3 **AND ROUTE** Attachment to the PNPS Senior Marine Fisheries Biologist.
- [5] **RECORD** the duplicate sample results in LABSTATS or equivalent.

9.0 ACCEPTANCE CRITERIA

Refer to PNPS 7.8.1.

10.0 ATTACHMENTS

ATTACHMENT 1 - FORM CH-43, TOTAL RESIDUAL CHLORINE IN DISCHARGE CANAL

ATTACHMENT 2 - WEEKLY CHLORINE STANDARD CHECK

ATTACHMENT 3 - SAMPLE DURING THERMAL BACKWASH

ATTACHMENT 4 - DETERMINATION OF SCREENWASH TOTAL RESIDUAL CHLORINE

CH-43

TOTAL RESIDUAL CHLORINE IN DISCHARGE CANAL

Date of Analysis _____ Method of Communication _____

Personnel: Chem Tech _____ Operator _____

NOTES

1. A waiting period shall be observed prior to any increase in the hypo injection rate. The length of time is dependent upon the CW (seawater) pumps in service and shall be as follows:
 - 2 CW pumps operating, then wait at least 20 minutes between increases.
 - 1 CW pump operating, then wait at least 40 minutes between increases.
2. When only one CW pump is in service, do not perform CW hypo injection unless both conditions below are met:
 - a. Both SM and Chemistry Superintendent permission obtained.
 - b. Seas less than 2 feet near the mouth of the discharge canal.
3. Record routine data from hypo injection and TRC analysis on Sheet 2. Some of this info must be obtained from the Operator controlling injection.
4. Samples should be taken every 10 to 15 minutes.

Shorefront pH Instr. Number: _____

Lab pH Instr. Number: _____

Thermometer or Temperature Probe Number: _____

	pH	Temp (°F)	Duplicate (Select one)	Tech Signature/Date/Time	
Intake					
Discharge					
Screenwash					
Screenwash TRC	_____ mg/L		Time _____	Date _____	Tech _____

Chemistry Supervisor Review _____ Date _____

CH-43

TOTAL RESIDUAL CHLORINE IN DISCHARGE CANAL

CW Hypo Injection:

Started at _____ using Hypo Pump P-113A/B

Date of Analysis _____

Finished at _____ using Hypo Pump P-113A/B

Titration Functional Check:
SAT / UNSAT (circle one)

Data from Hypo Injection and Total Residual Chlorine (TRC) Analysis

Sample Time	Elapsed Time (minutes)	Hypo Pump Setting	Injection Rate (GPM)	Chlorine Conc. (ppm TRC)	Analysis Time	Remarks/Comments
	0 min.					
	10 min.					
	20 min.					
	30 min.					
	40 min.					
	50 min.					
	60 min.					
	10 min.					
	20 min.					
	30 min.					
	40 min.					
	50 min.					
	60 min.					
	+10 min.					
	+20 min.					
	Duplicate	_____	_____			
* DAILY AVERAGE						
* DAILY MAXIMUM						

* Exclude the TRC reading taken at time zero (0 min.) from these calculations.

Chemistry Technician

Chemistry Supervisor

Date

WEEKLY CHLORINE STANDARD CHECK

Date of Analysis _____ Date Standard Prepared _____
Chem Tech _____

NOTE

Results of weekly checks should be recorded on an instrument control chart.

- [1] Once a week, **PERFORM** a 0.10 ppm chlorine standard check on each amperometric titrator in use.
- [2] To prepare standard, **USE** a 1000 mL volumetric flask **AND ADD** 5 mL Standard A (or 0.5 mL Standard B), 5 mL iodide standard, and 5 mL acid standard.
- [3] **STOPPER** the flask **AND SWIRL** for 2 minutes to allow complete reaction.
- [4] **DILUTE** to 1000 mL with demineralized water **AND THOROUGHLY MIX**.
- [5] **ANALYZE** the standard **TWICE** in accordance with Section 8.2 of the base document. **RECORD** results below **AND SUBMIT** form to Supervisor for review.
- [6] The standard check should be 0.10 (0.09 to 0.11) ppm. **IF** results are outside this range, **INVESTIGATE** cause (i.e., prepare new standard, clean cell, change out titrant, etc.). **IF** results are still unsatisfactory, **CONTACT** Chemistry Supervision.

Results of Standard Check(s)

Instr. Number:	
Instr. Location:	
0.1 ppm Chlorine Std Check	
First Analysis	ppm
Second Analysis	ppm
Average	

Instr. Number:	
Instr. Location:	
0.1 ppm Chlorine Std Check	
First Analysis	ppm
Second Analysis	ppm
Average	

Comments _____

Chemistry Technician _____ Date _____

Chemistry Supervisor _____ Date _____

SAMPLE DURING THERMAL BACKWASH

DUPLICATE

DATE _____	
TIME _____	
pH _____	pH _____

SAMPLE OUTSIDE OF THERMAL BACKWASH

DUPLICATE

DATE _____	
TIME _____	
pH _____	pH _____

Within PNPS 7.8.1 Control Limit (Yes/No) _____

If "No", notify SM and Chemistry Supervisor and write CR.

Complete notification (Yes/N/A) _____

CHEMISTRY TECHNICIAN _____

CHEMISTRY SUPERVISOR _____

Route to the PNPS Senior Marine Fisheries Biologist

DETERMINATION OF SCREENWASH TOTAL RESIDUAL CHLORINE

- [1] **ENSURE** Titrator Functional Daily Check completed in accordance with PNPS 7.3.41.
- [2] **ENSURE** Weekly Chlorine Standard Check completed in accordance with PNPS 7.3.41.
- [3] **RINSE** beaker (titrator cup) with sample or fresh water.
- [4] **PLACE** 200 mL of sample in beaker **AND POSITION** beaker on titrator.
- [5] **TURN** rotary switch to the "mg/L" position.

NOTE

Always add potassium iodide first and then pH 4 buffer. These reagents may be added when sample is first collected or at this time, but not twice.

- [6] **IF** not done already, **ADD** 1 mL of potassium iodide solution.
- [7] **IF** not done already, **ADD** 1 mL pH 4 buffer solution.
- [8] **IF** necessary, **ADJUST** meter with the turns-counting dial so the meter needle is near 100.
- [9] **OBSERVE** initial titrant level on the pipet. **ADD** PAO (phenylarsine oxide solution) from the pipet in small increments (0.01 or 0.02 mL) by turning the stopcock counterclockwise while watching needle on meter for downward deflection.
 - (a) End point is just passed when the addition of a small increment of titrant no longer deflects the needle to the left. **DO NOT** count this last amount in the volume titrated. **IF** during the course of adding titrant the needle deflects below zero, **BRING** it back on scale by adjusting the turns-counting dial.

- [10] **WHEN** titration is finished, **OBSERVE** the titrant level in the pipet. Since ppm total residual chlorine (TRC) equals mL titrated, **CALCULATE** the difference between the initial and final pipet readings. **IF** after adding 0.05 mL of titrant there has been no needle deflection, **ENTER** 0.00 under "TRC level (ppm)" (**OTHERWISE**, **ENTER** mL titrated) into database.
- [11] **IF** TRC is greater than Achievable Limit of PNPS 7.8.1, **NOTIFY** Operations to secure screenwashing **AND INVESTIGATE** dechlorination injection.
- [12] **DISPOSE** of sample. **RINSE** beaker and electrode with fresh water. **STORE** cell in fresh water.
- [13] **ENTER** analysis results into Chemistry database and Attachment 1.