## PHILADELPHIA ELECTRIC COMPANY

NUCLEAR GROUP HEADQUARTERS 955-65 CHESTERBROOK BLVD. WAYNE, PA 19087-5691 (215) 640-6000

NUCLEAR ENGINEERING & SERVICES DEPARTMENT

May 21, 1991

Docket Nos. 50-352 50-353

License Nos. NPF-39

NPF-85

U.S. Nuclear Regulatory Commission Attn: Document Control Desk Washington, DC 20555

Subject: Limerick Generating Station, Units 1 and 2 Proposed Change to the National Pollutant Discharge Elimination System Permit

Gentlemen:

The Limerick Generating Station (LGS), Units 1 and 2, Environmental Protection Plan (EPP), Section 3.2, stipulates that the NRC shall be receive a copy of any proposed change to the LGS National Pollutant Discharge Elimination System (NPDES) permit at the same time the proposed change is submitted to the permitting agency.

By letter dated May 1, 1991 to the Pennsylvania Department of Environmental Resources (PA DER), Philadelphia Electric Company (PECo) requested a change to the LGS NPDES Permit No. PA0051926 to allow for the addition of new chemical additives for use in the secondary cooling water to control Asiatic clams. The PA DER had previously authorized the use of these new chemicals at our Peach Bottom Atomic Power Station facility to inhibit Asiatic clam fouling of their secondary cooling water systems.

Therefore, in accordance with the LGS EPP Section 3.2, a copy of the May 1, 1991 letter to the PA DER (including attachments) requesting the change to the LGS NPDES permit is enclosed.

9105310197 910521 PDR ADOCK 05000352 PDR PDR If you have any questions, please do hesitate to contact us.

Very truly yours,

Georph

G. J. Beck Manager Licensing Section Nuclear Engineering and Services

Enclosure

cc: T. T. Martin, Administrator, Region I, USNRC (\*/ enclosure) T. J. Kenny, USNRC Senior Resident Inspector, .GS w/ enclosure) ENCLOSURE

## PHILADELPHIA ELECTRIC COMPANY

2301 MARKET STREET P. O. BOX 8699 PHILADELPHIA, PA 19101 (215) 841-4000 G. J. BECK LICENSING SECTION

MAY 0 6 1991

REFERRED TO: OTMA

May 1, 1991

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Mr. James Newbold Chief, Permits Section Bureau of Water Quality Management Lepartment of Environmental Resources Lee Fark, Suite 6010 555 North Lane Conshohocken, PA 19428

R: Limerick Generating Station, NPDES Permit PA0051926 Request for Use of New Chemicals for Control of Asiatic Clams

De ar Mr. Newbold:

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In accordance with Chapter 92.7 "Reporting of New or /.creased Discharges", of the Department's Rules and Regulations, we hereby request approval to use Betz Clam-troi CT-1, Betz Foamtrol CT and Betz DTS in the cooling water systems at Limerick Generating Station (LGS), discharge point 001. These Betz chemicals will be used in concert with each other to control Asiatic clams.

Asiatic clams have caused substantial water system problems throughout the utility industry, including Peach Bottom Atomic Fower Station (PEAPS). Once they have entered into plant cooling water systems, they can reproduce and grow, causing severe flow restrictions. These events have resulted in increased NRC concern, most notably through Generic Letter 89-13. This letter requires utilities to develop some mechanism to prevent this type of flow blockage. Makeup water screening has little effect, as larval clams are too small to screen, and standard chlorination practices restricted by regulation do not permit sufficient chemical contact time. Asiatic clams have existed in the Schuylkill River for years. They have now progressed to areas near LGS intakes, and thus pose a threat to plant reliability and operation.

To prevent plant problems, we wish to begin a biocide program similar to that used successfully at other facilities. In our Generic Letter 89-13 response to the NRC, we indicated that this would be our course of action, provided that environmental concerns could be resolved. We would apply Betz CT-1 to both cooling towers, and directly to the safety-related service water systems that take suction from the spray pond. Each cooling Mr. James Newbold May 1, 1991

tower/service water system is expected to be treated 2 times per year, but more frequent applications are possible. The duration of treatment should be approximately 24 hours per system. Normal CT-1 concentrations should be 15 ppm; however, concentrations of 50 ppm may be used when it is necessary to "lay up" components with treated water. Due to the number of systems involved, and chemical holding times within those systems, CT-1 could enter the plant discharge for up to 2 weeks per application.

To preclude the discharge of CT-1 to the river, we intend to feed Betz DTS, a 23% bentonite clay slurry, to the blowdown line (discharge 001) whenever Betz CT-1 residual would exist in the cooling tower blowdown. Approximately five (5) ppm of this slurry would be fed for every 1 ppm of CT-1 entering in discharge 001. Betz DTS, as well as existing solids in the water, will detoxify the active ingredients in CT-1. As a monitoring requirement, we propose that, during treatment, the level of CT-1 should be verified to be less than 0.2 ppm at discharge point 001 once per day. This value represents the lower limit of detection for the CT-1 test method.

Betz DTS is a non-toxic agent used to detoxify Betz CT-1. Should a total suspended solids limit be required due to this additive, a net limitation would be appropriate since the cooling tower blowdown already contains TSS from the Schuylkill River. The Steam Electric Effluent Guidelines contained in 40 CFR Part 423 indicated that a net TSS limitation of 30 mg/l and 100 mg/l, monthly average and daily maximum, respectively, may be applied.

Since CT-1 does have some surfactant qualities, foaming in cooling tower systems could result. In preparation, we also request approval of Betz Foamtrol CT to control foaming if necessary. This product is essentially non-toxic, and would be applied at a 10 ppm concentration <u>directly</u> to the areas of foaming. Thus, when used in this fashion, we do not expect detectable levels of Foamtrol CT in the blowdown.

Based on the current status of Schuylkill River clam populations, we feel that we will need to begin treatments in mid-June 1991. The application of this treatment will be controlled by written plant procedures, and oversight will be provided by Betz personnel familiar with the applications at other facilities. Furthermore, we intend to minimize chemical discharges by decreasing cooling tower blowdown as much as possible. Technical information regarding the products is attached. For additional information, it would be best to contact Steve Jordon, of Betz Industrial, at 215-524-6080. Although we could conceivably pursue the use of equivalent products at some time in the future, (similar to our current intent regarding cooling tower chemicals), it is not likely due to existing U.S. patent concerns. Therefore, the permit amendment can be specific to the Betz products. Mr. James Newbold May 1, 1991

If there are any questions, please call David Mobraaten at (215) 841-5679.

Very truly yours,

Decige M Marly

George M. Morley Director Environmental Affairs

DWM/lth Attachments bcc: J. M. Madara, Jr. w/o attachment G. M. Leitch " " J. Doering, Jr. " " J. Doering, Jr. w/attachment w/ " R. W. Dubiel G. J. Madsen G. J. Beckv R. J. Scholz w/ 11 W/ 11 . 6 CCD w/ 11 PaDER BRP Inspector w/

BETZ LABORATORIES, INC. 4636 SOMERTON ROAD, TREVOSE, PA. 19047

PRODUCT: BETZ DTS

4/15/91 AQUATIC TOXICOLOGY

DAPHNIA MAGNA

3

0% MORTALITY: 435 MG/L 48 HR. SCR. FATHEAD MINNOW

> 0% MORTALITY: 435 MG/L 96 HR. SCR.

> > 5.

4/15/91 MAMMALIAN TOXICOLOGY ORAL LD50 -NO DATA DERMAL LD50 -NO DATA SKIN IRRITATION SCORE-NO DATA EYE IRRITATION SCORE-NO DATA INHALATION-NO DATA BETZ LABORATORIES, INC. 4636 SOMERTON ROAD, TREVOSE, PA. 19047

& PRODUCT: FOAM-TROL CT

4/15/91 AQUATIC TOXICOLOGY

DAPHNIA MAGNA

1

0% MORIALITY: 100 MG/L 48 HR. SCR. BLUEGILL SUNFISH

> 0% MORTALITY: 1000 MG/L 48 HR. SCR.

4/15/91 MAMMALIAN TOXICOLOGY ORAL LD50 -NO DATA DERMAL LD50 -NO DATA SKIN IRRITATION SCORE-NO DATA EYE IRRITATION SCORE-NO DATA INHALATION-NO DATA

OXYGEN DEMAND (ppm) PRODUCT CONCENTRATION (ppm) BOD COD TOC 1000 249 1280 110

BETZ LABORATORIES, INC. 4636 SOMERTON ROAD, TREVOSE, PA. 19053 BETZ MATERIAL SAFETY DATA SHEET EMERGENCY TELEPHONE (HEALTH/ACCIDENT) 800-877-1940

3

PRODUCT : CLAM-TROL CT-1

(PAGE 1 OF 3) EFFECTIVE DATE 02-16-91 PRINTED: 1-Mar-1991 REVISIONS TO SECTIONS: -; EDIT: APPENDIX

PRODUCT APPLICATION : WATER-BASED MICROBIAL CONTROL AGENT. ----SECTION 1-----HAZARDOUS INGREDIENTS-----

INFORMATION ON PHYSICAL HAZARDS, HEALTH HAZARDS, PEL'S AND TLV'S FOR SPECIFIC PRODUCT INGREDIENTS AS REQUIRED BY THE OSHA HAZARD COMMUNICATIONS STANDARD IS LISTED. REFER TO SECTION 4 (PAGE 2) FOR OUR ASSESSMENT OF THE POTENTIAL ACUTE AND CHRONIC HAZARDS OF THIS FORMULATION. THIS PRODUCT IS SUBJECT TO THE PENNSYLVANIA AND NEW JERSEY WORKER AND COMMUNITY RIGHT TO KNOW LAW.

ETHYLENE GLYCOL\*\*\*CAS#107-21-1;LIVER, KIDNEY AND BLOOD TOXIN;CNS DEPRESSANT; ANIMAL TERATOGEN (HIGH ORAL DOSES); PEL/TLV: 50PPM-C.

ALKYL DIMETHYL BENZYL AMMONIUM CHLORIDE\*\*\*CAS#68424-85-1; CORROSIVE(EYES); PEL:NONE;TLV:NONE.

ISOPROPYL ALCOHOL (IPA) \*\*\*CAS#67-63-0;FLAMMABLE LIQUID;CHRONIC OVEREXPOSURE MAY CAUSE LIVER AND KIDNEY TOXICITY; PEL/TLV: 400PPM (500PPM-STEL).

DODECYLGUANIDINE HYDROCHLORIDE\*\*\*(DGH); CAS#13590-97-1; CORROSIVE; PEL: NONE; TLV:NONE.

ETHYL ALCOHOL (ETHANOL) \*\*\*CA5#64-17-5; FLAMMABLE; EYE IRRITANT; MAY CAUSE DEFATTING DERMATITIS, DIZZINESS AND HEADACHE; PEL/TLV: 1000PPM.

NONHAZARD INGREDIENTS: WATER(7732-18-5)

----SECTION 2-----TYPICAL PHYSICAL DATA-----PH: AS IS (APPROX.) 5.3 ODOR: MILD FL.PT. (DEG.F): 116 SETA(CC) SP.GR. (7QF) OR DENSITY: 1.022 VAPOR PRESSURE (mmHG): 23 VAPOR DENSITY (AIR=1): >1 VISC cps70F: 23 %SOLUBILITY(WATER): 100 EVAP.RATE: <1 ETHER=1 FREEZE POINT(DEG.F): <-30 PHYSICAL STATE: LIQUID ----SECTION 3-----REACTIVITY DATA---

STABLE.MAY LEACT WITH STRONG OXIDIZERS. DO NOT CONTAMINATE. BETZ TANK CLEAN-OUT CATEGORY 'B'

THERMAL DECOMPOSITION (DESTRUCTIVE FIRES) YIELDS ELEMENTAL OXIDES.

BETZ MATERIAL SAFETY DATA SHEET (PAGE 2 OF 3) PRODUCT: CLAM-TROL CT-1 ----SECTION 4----HEALTH HAZARD EFFECTS-----ACUTE SKIN EFFECTS \*\*\* PRIMARY ROUTE OF EXPOSURE CORROSIVE TO SKIN. POTENTIAL SKIN SENSITIZER ACUTE EYE EFFECTS \*\*\* CORROSIVE TO THE EYES ACUTE RESPIRATORY EFFECTS \*\*\* PRIMARY ROUTE OF EXPOSURE VAPORS, GASES, MISTS AND/OR AEROSOLS CAUSE IRRITATION TO UPPER RESPIRATORY TRACT CHRONIC EFFECTS OF OVEREXPOSURE\*\*\* PROLONGED OR REPEATED OVEREXPOSURES MAY CAUSE: TISSUE NECROSIS; BLOOD CELL DAMAGE OR IMPAIR BLOOD CELL FUNCTION; REPRODUCTIVE SYSTEM TOXICITY; SKIN SENSITIZATION. MEDICAL CONDITIONS AGGRAVATED \*\*\* NOT KNOWN SYMPTOMS OF EXPOSURE \*\*\* INHALATICN OF VAPORS/MISTS/AEROSOLS MAY CAUSE EYE, NOSE, THROAT AND LUNG IRRITATION; SKIN CONTACT MAY CAUSE SEVERE IRRITATION OR BURNS. PRECAUTIONARY STATEMENT BASED ON TESTING RESULTS \*\*\* MAY BE TOXIC IF ORALLY INGESTED. ---SECTION 5-----FIRST AID INSTRUCTIONS------SKIN CONTACT\*\*\* REMOVE CLOTHING. WASH AREA WITH LARGE AMOUNTS OF SOAP SOLUTION OR WATER FOR 15 MIN. IMMEDIATELY CONTACT PHYSICIAN EYE CONTACT\*\*\* IMMEDIATELY FLUSH EYES WITH WATER FOR 15 MINUTES. IMMEDIATELY CONTACT A PHYSICIAN FOR ADDITIONAL TREATMENT INHALATION EXPOSURE\*\*\* REMOVE VICTIM FROM CONTAMINATED AREA. APPLY NECESSARY FIRST AID TREATMENT. IMMEDIATELY CONTACT A PHYSICIAN. INGESTION\*\*\* DO NOT FEED ANYTHING BY MOUTH TO AN UNCONSCIOUS OR CONVULSIVE VICTIM DO NOT INDUCE VOMITING.IMMED.CONTACT PHYSICIAN.DILUTE COLLENTS OF STOMACH USING 3-4 GLASSES MILK OR WATER ----SECTION 6-----SPILL, DISPOSAL AND FIRE INSTRUCTIONS-----SPILL INSTRUCTIONS\*\*\* VENTILATE AREA, USE SPECIFIED PROTECTIVE EQUIPMENT. CONTAIN AND ABSORB ON ABSORBENT MATERIAL. PLACE IN WASTE DISPOSAL CONTAINER. THE CONTAMINATED ABSORBENT SHOULD BE CONSIDERED A PESTICIDE AND DISPOSED OF IN AN APPROVED PESTICIDE LANDFILL.SEE PRODUCT LABEL STORAGE AND DISPOSAL INSTRUCTIONS. REMOVE IGNITION SOURCES. FLUSH AREA WITH WATER. SPREAD SAND/GRIT. DISPOSAL INSTRUCTIONS\*\*\* WATER CONTAMINATED WITH THIS PRODUCT MAY BE SENT TO A SANITARY SEWER TREATMENT FACILITY, IN ACCORDANCE WITH ANY LOCAL AGREEMENT, A PERMITTED WASTE TREATMENT FACILITY OR DISCHARGED UNDER A NPDES PERMIT PRODUCT (AS IS) -DISPOSE OF IN APPROVED PESTICIDE FACILITY OR ACCORDING TO LABEL INSTRUCTIONS FIRE EXTINGUISHING INSTRUCTIONS\*\*\* FIREFIGHTERS SHOULD WEAR POSITIVE PRESSURE SELF-CONTAINED BREATHING APPARATUS (FULL FACE-PIECE TYPE). PROPER FIRE EXTINGUISHING MEDIA: DRY CHEMICAL, CARBON DIOXIDE, FOAM OR WATER

BETZ MATERIAL SAFETY DATA SHEET (PAGE 3 OF 3)

PRODUCT: CLAM-TROL CT-1

USE PROTECTIVE EQUIPMENT IN ACCORDANCE WITH 29CFR SECTION 1910.132-134. USE RESPIRATORS WITHIN USE LIMITATIONS OR ELSE USE SUPPLIED AIR RESPIRATORS. VENTILATION PROTECTION\*\*\*

ADEQUATE VENTILATION TO MAINTAIN AIR CONTAMINANTS BELOW EXPOSURE LIMITS RECOMMENDED RESPIRATORY PROTECTION\*\*\*

IF VENTILATION IS INADEQUATE OR SIGNIFICANT PRODUCT EXPOSURE IS LIKELY, USE A RESPIRATOR WITH ORGANIC VAPOR CARTRIDGE & DUST/MIST PREFILTER RECOMMENDED SKIN PROTECTION\*\*\*

GAUNTLET-TYPE RUBBER GLOVES, CHEMICAL RESISTANT APRON WASH OFF AFTER EACH USE.REPLACE AS NECESSARY

RECOMMENDED EYE PROTECTION\*\*\* SPLASH PROOF CHEMICAL GOGGLES.FACE SHIELD

-----SECTION 8-----STORAGE AND HANDLING PRECAUTIONS-----

STORAGE INSTRUCTIONS\*\*\*

KEEP DRUMS & PAILS CLOSED WHEN NOT IN USE.

STORE IN COOL VENTILATED LOCATION.STORE AWAY FROM OXIDIZERS HANDLING INSTRUCTIONS\*\*\*

COMBUSTIBLE. DO NOT USE AROUND SPARKS OR FLAMES. BOND CONTAINERS DURING FILLING OR DISCHARGE WHEN PERFORMED AT TEMPERATURES AT OR ABOVE THE PRODUCT FLASH POINT.

THE CONTENT OF THIS APPENDIX REPRESENTS INFORMATION KNOWN TO BETZ ON THE EFFECTIVE DATE OF THIS MSDS. THIS INFORMATION IS BELIEVED TO BE ACCURATE. ANY CHANGES IN REGULATIONS WILL RESULT IN UPDATED VERSIONS OF THIS DOCUMENT.

... TSCA: THIS IS AN EPA REGISTERED BIOCIDE AND IS EXEMPT FROM TSCA INVENTORY REQUIREMENTS

...FIFRA(40CFR):EPA REG.NO. 3876- 145

... REPORTABLE QUANTITY (RQ) FOR UNDILUTED PRODUCT:

NOT APPLICABLE

...RCRA: IF THIS PRODUCT IS DISCARDED AS A WASTE, THE RCRA HAZARDOUS WASTE IDENTIFICATION NUMBER IS: DO01=IGNITABLE;D002=CORROSIVE(SKIN) ...DOT HAZARD/UN#/ER GUIDE# IS: CORROSIVE TO SKIN.COMBUSTIBLE UN1760/#60 ...CALIFORNIA SAFE DRINKING WATER ACT (PROPOSITION 65) MATERIALS: NONE ...SARA SECTION 302 CHEMICALS: NONE ...SARA SECTION 313 CHEMICALS: ETHYLENE GLYCOL(107-21-1) , 21.0-30.0% ; ...SARA SECTION 312 HAZARD CLASS: IMMEDIATE(ACUTE),DELAYED(CHRONIC) AND FIRE ...MICHIGAN CRITICAL MATERIALS: NONE

NFPA/HMIS : HEALTH - 3 ; FIRE - 2 ; REACTIVITY - 0 ; SPECIAL - CORR ; PE - D

BETZ LABORATORIES, INC. 4636 SOMERTON ROAD, TREVOSE, PA. 19053 BETZ MATERIAL SAFETY DATA SHEET EMERGENCY TELEPHONE (HEALTH/ACCIDENT) 800-877-1940

PRODUCT : FOAM-TROL CT

(PAGE 1 OF 3) EFFECTIVE DATE 02-16-91 PRINTED: 1-Mar-1991 REVISIONS TO SECTIONS: -;EDIT:APPENDIX

PRODUCT APPLICATION : ANTIFOAM.

INFORMATION ON PHYSICAL HAZARDS, HEALTH HAZARDS, PEL'S AND TLV'S FOR SPECIFIC PRODUCT INGREDIENTS AS REQUIRED BY THE OSHA HAZARD COMMUNICATIONS STANDARD IS LISTED. REFER TO SECTION 4 (PAGE 2) FOR OUR ASSESSMENT OF THE POTENTIAL ACUTE AND CHRONIC HAZARDS OF THIS FORMULATION. THIS PRODUCT IS SUBJECT TO THE PENNSYLVANIA AND NEW JERSEY WORKER AND COMMUNITY RIGHT TO KNOW LAW.

MINERAL OIL(MILDLY SOLVENT-REFINED OR HYDROTREATED OILS)\*\* CAS#64742-30-9; POTENTIAL SKIN TUMORIGEN(BASED ON CHRONIC ANIMAL SKIN PAINTING STUDIES); PEL:5MG/M3;TLV:5MG/M3.

NONHAZARD INGREDIENTS: POLYPROPYLENE GLYCOL GLYCEROL ETHER(25791-96-2) ; OCTADECANOIC ACID(57-11-4) ; POLYETHYLENE GLYCOL MONOOLEATE(61791-00-2)

TYPICAL	PHYSICAL DATA
PH: 50% SOL. (APPROX.) 6.8	ODOR: MILD
FL.PT. (DEG.F): >200 SETA(CC)	SP.GR. (70F)OR DENSITY: 0.841
VAPOR PRESSURE (mmHG): <10	VAPOR DENSITY(AIR=1): >1
VISC cps70F: 30	%SOLUBILITY (WATER) : 0
EVAP.RATE: <1 ETHER=1	APPEARANCE: OFF WHITE TO AMBER
PHYSICAL STATE: LIQUID	FREEZE POINT(DEG.F): ND
REACTIVI	TY DATA

STABLE.MAY REACT WITH STRONG OXIDIZERS.DO NOT CONTAMINATE.BETZ TANK CLEAN-OUT CATEGORY 'B'

THERMAL DECOMPOSITION (DESTRUCTIVE FIRES) YIELDS ELEMENTAL OXIDES.

BETZ MATERIAL SAFETY DATA SHEET (PAGE 2 OF 3) PRODUCT: FOAM-TROL CT ----SECTION 4-----HEALTH HAZARD EFFECTS----and any set was been any our bar and the set of the set ACUTE SKIN EFFECTS \*\*\* PRIMARY ROUTE OF EXPOSURE SLIGHTLY IRRITATING TO THE SKIN. MAY CAUSE DERMATITIS. ACUTE EYE EFFECTS \*\*\* MODERATELY IRRITATING TO THE EYES ACUTE RESPIRATORY EFFECTS \*\*\* VAPORS, GASES MISTS AND/OR AEROSOLS MAY CAUSE IRRITATION TO UPPER RESPIRATORY TRACT CHRONIC EFFECTS OF OVEREXPOSURE\*\*\* PROLONGED OR REPEATED EXPOSURES MAY CAUSE DEFATTING-TYPE DERMATITIS: LIFETIME SKIN PAINTING STUDIES IN MICE HAVE PRODUCED SKIN TUMORS. MEDICAL CONDITIONS AGGRAVATED \*\*\* NOT KNOWN SYMPTOMS OF EXPOSURE \*\*\* PROLONGED EXPOSURE MAY CAUSE DRYING AND CRACKING OF SKIN. - ---SECTION 5-----FIRST AID INSTRUCTIONS-----SKIN CONTACT\*\*\* REMOVE CONTAMINATED CLOTHING. WASH EXPOSED AREA WITH A LARGE QUANTITY OF SOAP SOLUTION OR WATER FOR 15 MINUTES EYE CONTACT \*\*\* IMMEDIATELY FLU H EYES WITH WATER FOR 15 MINUTES. IMMEDIATELY CONTACT A PHYSICIAN FOR ADDITIONAL TREATMENT INHALATION EXPOSURE\*\*\* REMOVE VICTIM FROM CONTAMINATED AREA TO FRESH AIR. APPLY APPROPRIATE FIRST AID TREATMENT AS NECESSARY INGESTION\*\*\* DO NOT FEED ANYTHING BY MOUTH TO AN UNCONSCIOUS OR CONVULSIVE VICTIM DO NOT INDUCE VOMITING. IMMED. CONTACT PHYSICIAN. DILUTE CONTENTS OF STOMACH USING 3-4 GLASSES MILK OR WATER -----SECTION 6-----SPILL, DISPOSAL AND FIRE INSTRUCTIONS------SPILL INSTRUCTIONS\*\*\* VENTILATE AREA, USE SPECIFIED PROTECTIVE EQUIPMENT. CONTAIN AND ABSORB ON ABSORBENT MATERIAL. PLACE IN WASTE DISPOSAL CONTAINER. THE WASTE CHARACTERISTICS OF THE ABSORBED MATERIAL, OR ANY CONTAMINATED SOIL, SHOULD BE DETERMINED IN ACCORDANCE WITH RCRA REGULATIONS. FLUSH AREA WITH WATER. WET AREA MAY BE SLIPPERY. SPREAD SAND/GRIT. DISPOSAL INSTRUCTIONS\*\*\* WATER CONTAMINATED WITH THIS PRODUCT MAY BE SENT TO A SANITARY SEWER TREATMENT FACILITY, IN ACCORDANCE WITH ANY LOCAL AGREEMENT, A PERMITTED WASTE TREATMENT FACILITY OR DISCHARGED UNDER A NPDES PERMIT PRODUCT (AS IS) -INCINERATE OR BURY IN APPROVED LANDFILL FIRE EXTINGUISHING INSTRUCTIONS\*\*\* FIREFIGHTERS SHOULD WEAR POSITIVE PRESSURE SELF-CONTAINED BREATHING APPARATUS (FULL FACE-PIECE TYPE) . PROPER FIRE EXTINGUISHING MEDIA: DRY CHEMICAL/CO2/FOAM OR WATER. SLIPPERY CONDITION. USE SAND/GRIT

BETZ MATERIAL SAFETY DATA SHEET (PAGE 3 OF 3)

PRODUCT: FOAM-TROL CT

----SECTION 7-----SPECIAL PROTECTIVE EQUIPMENT-----USE PROTECTIVE EQUIPMENT IN ACCORDANCE WITH 29CFR SECTION 1910.132-134. USE RESPIRATORS WITHIN USE LIMITATIONS OF ELSE USE SUPPLIED AIR RESPIRATORS. VENTILATION PROTECTION \*\*\* ADEQUATE VENTILATION TO MAINTAIN AIR CONTAMINANTS BELOW EXPOSURE LIMITS RECOMMENDED RESPIRATORY PROTECTION\*\*\* IF VENTILATION IS INADEQUATE OR SIGNIFICANT PRODUCT EXPOSURE IS LIKELY, USE A RESPIRATOR WITH ORGANIC VAPOR CARTRIDGES. RECOMMENDED SKIN PROTECTION\*\*\* NEOPRENE GLOVES WASH OFF AFTER EACH USE. REPLACE AS NECESSARY RECOMMENDED EYE PROTECTION\*\*\* SPLASH PROOF CHEMICAL GOGGLES ----SECTION 8-----STORAGE AND HANDLING PRECAUTIONS-----STORAGE INSTRUCTIONS\*\*\* KEEP DRUMS & PAILS CLOSED WHEN NOT IN USE. STORE IN COOL VENTILATED LOCATION.STORE AWAY FROM OXIDIZERS HANDLING INSTRUCTIONS\*\*\* NORMAL CHEMICAL HANDLING \*\*\*\*\*\*\*\* THIS MSDS WAS WRITTEN TO COMPLY WITH THE OSHA HAZARD COMMUNICATION STANDARD APPENDIX: REGULATORY INFORMATION THE CONTENT OF THIS APPENDIX REPRESENTS INFORMATION KNOWN TO BETZ ON THE EFFECTIVE DATE OF THIS MSDS. THIS INFORMATION IS BELIEVED TO BE ACCURATE. ANY CHANGES IN REGULATIONS WILL RESULT IN UPDATED VERSIONS OF THIS DOCUMENT. ... TSCA: ALL COMPONENTS OF THIS PRODUCT ARE LISTED ON THE TSCA INVENTORY ... REPORTABLE QUANTITY (RQ) FOR UNDILUTED PRODUCT: TREAT AS OIL SPILL ... RCRA: IF THIS PRODUCT IS DISCARDED AS A WASTE, THE RCRA HAZARDOUS WASTE IDENTIFICATION NUMBER IS: NOT APPLICABLE ... DOT HAZARD/UN#/ER GUIDE# IS: NOT APPLICABLE ... CALIFORNIA SAFE DRINKING WATER ACT (PROPOSITION 65) MATERIALS: THIS PRODUCT CONTAINS THESE CHEMICALS KNOWN TO THE STATE OF CALIFORNIA TO CAUSE CANCER OR REPRODUCTIVE TOXICITY: MINERAL OIL(64742-30-9) ... SARA SECTION 302 CHEMICALS: NONE ... SARA SECTION 313 CHEMICALS: NONE ... SARA SECTION 312 HAZARD CLASS: DELAYED(CHRONIC) ... MICHIGAN CRITICAL MATERIALS: NONE NFPA/HMIS : HEALTH - 1 ; FIRE - 1 ; REACTIVITY - 0 ; SPECIAL - NONE ; PE - B

BETZ LABORATORIES, INC. 4636 SOMERTON ROAD, TREVOSE, PA. 19053 BETZ MATERIAL SAFETY DATA SHEET EMERGENCY TELEPHONE (HEALTH/ACCIDENT) 800-877-1940

PRODUCT : BETZ DTS

(PAGE 1 OF 3) EFFECTIVE DATE 02-16-91 PRLATED: 15-Apr-1991

PRODUCT APPLICATION : A DETOXIFYING AGENT.

INFORMATION ON PHYSICAL HAZARDS, HEALTH HAZARDS, PEL'S AND TLV'S FOR SPECIFIC PRODUCT INGREDIENTS AS REQUIRED BY THE OSHA HAZARD COMMUNICATIONS STANDARD IS LISTED. REFER TO SECTION 4 (PAGE 2) FOR OUR ASSESSMENT OF THE POTENTIAL ACUTE AND CHRONIC HAZARDS OF THIS FORMULATION. THIS PRODUCT IS SUBJECT TO THE PENNSYLVANIA AND NEW JERSEY WORKER AND COMMUNITY RIGHT TO KNOW LAW.

SODIUM MONTMORILLONITE\*\*\*CAS#1302-78-9;POSSIBLE CHRONIC LUNG HAZARD;QUARTZ (PEL:10MG/M3/(Si02+2) RESP;TLV:0.1MG/M3 RESP); NOTE-TRIDYMITE & CRISTOBALITE(PELs&TLVs:1/2 QUARTZ VALUES) MAY BE PRESENT.

NONHAZARD INGREDIENTS: WATER(7732-18-5) ; 2-PROPENOIC ACID, HOMGPOLYMER(9003-01-4) ; SODIUM TRIPOLYPHOSPHATE(7758-29-4)

STABLE. BETZ TANK CLEAN-OUT CATEGORY 'B'

THERMAL DECOMPOSITION (DESTRUCTIVE FIRES) YIELDS ELEMENTAL OXIDES.

BETZ MATERIAL SAFETY DATA SHEET (PAGE 2 OF 3) PRODUCT: BETZ DTS -----SECTION 4-----HEALTH HAZARD EFFECTS-----ACUTE SKIN EFFECTS \*\*\* PRIMARY ROUTE OF EXPOSURE SLIGHTLY IRRITATING TO THE SKIN ACUTE EYE EFFECTS \*\*\* MODERATELY IRRITATING TO THE FYES ACUTE RESPIRATORY EFFECTS \*\*\* MISTS/AEROSOLS MAY CAUSE IRRITATION TO UPPER RESPIRATORY TRACT CHRONIC EFFECTS OF OVEREXPOSURE\*\*\* NO EVIDENCE OF POTENTIAL CHRONIC EFFECTS. MEDICAL CONDITIONS AGGRAVATED \*\*\* NOT KNOWN SYMPTOMS OF EXPOSURE \*\*\* MAY CAUSE REDNESS OR ITCHING OF SKIN. -----SECTION 5-----FIRST AID INSTRUCTIONS-----SKIN CONTACT\*\*\* REMOVE CONTAMINATED CLOTHING, WASH EXPOSED AREA WITH A LARGE QUANTITY OF SOAP SOLUTION OR WATER FOR 15 MINUTES EYE CONTACT\*\*\* IMMEDIATELY FLUSH EYES WITH WATER FOR 15 MINUTES. IMMEDIATELY CONTACT A PHYSICIAN FOR ADDITIONAL TREATMENT INHALATION EXPOSURE\*\*\* REMOVE VICTIM FROM CONTAMINATED AREA TO FRESH AIR. APPLY APPROPRIATE FIRST AID TREATMENT AS NECESSARY INGESTION\*\*\* DO NOT FEED ANYTHING BY MOUTH TO AN UNCONSCIOUS OR CONVULSIVE VICTIM DILUTE CONTENTS OF STOMACH. INDUCE VOMITING BY ONE OF THE STANDARD METHODS. IMMEDIATELY CONTACT & PHYSICIAN ----SECTION 6-----SPILL, DISPOSAL AND FIRE INSTRUCTIONS------SPILL INSTRUCTIONS\*\*\* VENTILATE AREA, USE SPECIFIED PROTECTIVE EQUIPMENT. CONTAIN AND ABSORB ON ABSORBENT MATERIAL. PLACE IN WASTE DISPOSAL CONTAINER. THE WASTE CHARACTERISTICS OF THE ABSORBED MATERIAL, OR ANY CONTAMINATED SOIL, SHOULD BE DETERMINED IN ACCORDANCE WITH RCRA REGULATIONS. FLUSH AREA WITH WATER, WET AREA MAY BE SLIPPERY. SPREAD SAND/GRIT. DISPOSAL INSTRUCTIONS\*\*\* WATER CONTAMINATED WITH THIS PRODUCT MAY BE SENT TO A SANITARY SEWER TREATMENT FACILITY, IN ACCORDANCE WITH ANY LOCAL AGREEMENT, A PERMITTED WASTE TREATMENT FACILITY OR DISCHARGED UNDER A NPDES PERMIT PRODUCT(AS IS) -INCINERATE OR BURY IN APPROVED LANDFILL FIRE EXTINGUISHING INSTRUCTIONS\*\*\* FIREFIGHTERS SHOULD WEAR POSITIVE PRESSURE SELF-CONTAINED BREATHING APPARATUS (FULL FACE-PIECE TYPE) . PROPER FIRE EXTINGUISHING MEDIA: DRY CHEMICAL, CARBON DIOXIDE, FOAM OR WATER

#### BETZ MATERIAL SAFETY DATA SHEET (PAGE 3 OF 3)

PRODUCT: BETZ DTS

----SECTION 7-----SPECIAL PROTECTIVE EQUIPMENT------USE PROTECTIVE EQUIPMENT IN ACCORDANCE WITH 29CFR SECTION 1910.132.134. USE RESPIRATORS WITHIN USE LIMITATIONS OR ELSE USE SUPPLIED AIR RESPIRATORS. VENTILATION PROTECTION\*\*\* ADEQUATE VENTILATION TO MAINTAIN AIR CONTAMINANTS BELOW EXPOSURE LIMITS RECOMMENDED RESPIRATORY FROTECTION\*\*\* IF VENTILATION IS INADEQUATE OR SIGNIFICANT PRODUCT EXPOSURE IS LIKELY, USE A RESPIRATOR WITH DUST/MIST FILTERS. RECOMMENDED SKIN PROTECTION\*\*\* F/BBER GLOVES WASH OFF AFTER EACH USE.REPLACE AS NECESSARY RECOMMENDED EYE PROTECTION\*\*\* SPLASH PROOF CHEMICAL GOGGLES

----SECTION 8-----STORAGE AND HANDLING PRECAUTIONS-----

STORAGE INSTRUCTIONS\*\*\*

KEEP DRUMS & PAILS CLOSED WHEN NOT IN USE.

DO NOT FREEZE. IF FROZEN, THAW AND MIX COMPLETELY PRIOR TO USE

HANDLING INSTRUCTIONS\*\*\* NORMAL CHEMICAL HANDLING

APPENDIX: REGULATORY INFORMATION

THE CONTENT OF THIS APPENDIX REPRESENTS INFORMATION KNOWN TO BETZ ON THE EFFECTIVE DATE OF THIS MSDS. THIS INFORMATION IS BELIEVED TO BE ACCURATE. ANY CHANGES IN REGULATIONS WILL RESULT IN UPDATED VERSIONS OF THIS DOCUMENT.

... TSCA: ALL COMPONENTS OF THIS PRODUCT ARE LISTED ON THE TSCA INVENTORY ... REPORTABLE QUANTITY (RQ) FOR UNDILUTED PRODUCT: TREAT AS OIL SPILL

...RCRA: IF THIS PRODUCT IS DISCARDED AS A WASTE, THE RCRA HAZARDOUS WASTE IDENTIFICATION NUMBER IS: NOT APPLICABLE

...DOT HAZARD/UN#/ER GUIDE# IS: NOT APPLICABLE

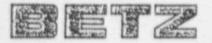
... CALIFORNIA SAFE DRINKING WATER ACT (PROPOSITION 65) MATERIALS: NONE ... SARA SECTION 302 CHEMICALS: NONE

... SARA SECTION 313 CHEMICALS: NONE

... SARA SECTION 312 HAZARD CLASS: IMMEDIATE(ACUTE)

...MICHIGAN CRITICAL MATERIALS: NONE

NFPA/HMIS : HEALTH - 1 ; FIRE - 1 ; REACTIVITY - 0 ; SPECIAL - NONE ; PE - B



LABORATORIES, INC.



SOMERTON ROAD+TREVOSE, PA 19047+U.S.A. / TEL: 215+355-3300+TELEX: 173 148+FAX # 355-2869

#### ENVIRONMENTAL INFORMATION ON CLAM-TROL CT-1 FOR ZEERA MUSSEL AND ASIATIC CLAM FOULDING CONTROL

Clam-Trol CT-1 is a patented nonoxidizing molluscicide providing state-of-the-art control for macrofouling caused by Asiatic clams, Zebra mussels and marine fouling organisms. Clam-Trol CI-1 is a federally registered molluscicide for use in once-through and recirculating cooling systems. The EPA registration number for CT-1 is 3876-145.

Clam-Trol CT-1 has been used in the past 4 years for Asiatic clam macrofouling control to power plants, steel mills, chemical refineries and other manufacturing facilities. Appendix A presents some case histories for Asiatic clam control.

The efficacy of CT-1 towards zebra mussels has been demonstrated in laboratory studies and it has also been utilized for the extermination of zebra mussels at two power plants near Detroit in November/December 1989. The laboratory evaluations (See Appendix B) demonstrated the efficacy of CT-1 for exposure periods of 6 hrs to 24 hrs at water temperatures of 5°, 10°, 15° and 20°C. It has been demonstrated that mortality responses are dependent upon CT-1 dosage, exposure period, and temperature.

The performance of the CT-1 in the extermination of zebra mussels at the J. R. Whiting Power Plant and the Fermi II Nuclear Power Plant has been presented at several conferences in 1990 (See Appendix C). These 12 to 15 hour applications were monitored for zebra mussel mortalities using flow through side stream bioboxes. Mortality responses ranged from greater than 95% at the outlet of the condensers wher water temperatures were 14° to 17°C to 25-35% at the inlet ends with colder temperatures of 2° to 6°C. CT-1 treatments or 6 to 8 hr being applied to cooling systems during the Summer of 1990 when water temperatures were above 20 °C achieved 80 to 100% mussel eradication. Recommendations for optimizing Clam-Trol CT-1 applications for Zebra mussel control and meeting discharge permitting requirements are presented in this publication.

Information on Clam-Trol CT-1 to aid in addressing NPDES permit requirements is being presented, as follows:

1. Name of the additive

Clam-Trol CT-1 contains 13% active ingredients (two cationic



surfactants) and 87% inert materials. The two cationic surfactants are N-alkyl dimethylbenzyl ammonium chloride (Quat) and dolecylguanidine hydrochloride (DGH). The inert materials of this formulation - ethylene glycol, isopropyl alcohol and water relatively nontoxic to aquatic organisms.

2. Concentration (mg/l) of the additive to be used:

Clam-Trol CT-1 is usually fed at concentrations ranging from 10 mg/l to 25 mg/l. The concentration to be fed will primarily depend upon the demand of the cooling system, resulting in passive neutralization of the CT-1 actives. The length of the exposure period will vary from 6 hours to 24 hours depending upon the water temperature and the CT-1 dosage.

Either seasonal or bimonthly treatment programs ranging from 2 to 6 times/year is required for macrofouling control of either zebra mussels or Asiatic clams. It must be noted that the objective of these seasonal or bimonthly applications is to provide a preventative treatment program by exterminating the juvenile mollusks to prevent their growth to adult fouling size and to reduce the overall accumulation of juvenile mollusks setting within cooling systems.

Each cooling system will have a specific treatment program to meet the macrofouling control requirements for that facility. The frequency of the applications, ranging from 2 to 6 times/year, will depend upon the degree of larvae and juvenile mollusk infestations and the kind of macrofouling control so the operations of the power plant or industrial facility is not impeded.

 Expected concentration of the additive contained in the discharge or blowdown immediately prior to entering state surface waters:

All seasonal or bimonthly CT-1 treatment programs are designed so that the concentration of Clam-Trol CT-1 is always less than 1 mg/l in the discharge. The reduction of CT-1 from the point-of-feed to less than 1. mg/l at the cutfall is achieved by one or more of the following approaches:

 Both the intake river w ler and the cooling system have many kinds of naturally occurring materials - silts, clays, suspended solids, humic acids, and the microfouled surfaces of cooling pipes - that will exert a demand upon the CT-1 actives. Both actives (Quat and DGH) will readily adsorb to these materials. Once adsorbed they no longer exhibit toxicity. Thus the passive neutralization of the CT-1 actives as they pass through the cooling [Astem will significantly reduce the concentration prior to discharge.



- 2) Many Clam-Trol CT-1 treatment programs focus upon segmented applications where only a portion of the total cooling water is being treated at any one time. This segmented treatment approach allows for the dilution and passive neutralization of the treated water with the remaining untreated cooling water. This segmented treatment approach can often achieve CT-1 concentrations of less than 1 mg/1.
- 3) If necessary, Clam-Trol CT-1 applications can be actively detoxified by feeding a blend of clays prior to discharge. Clays are fed at a ratio of 1 mg/1 of clay for each 1 mg/l of CT-1 to be detoxified to achieve discharge concentrations of less than 1 mg/l.
- 4) An analytical photometric method is available for monitoring the concentration of CI-1. This field method has a sensitivity of 0.2 mg/l. (Appendix J)
- Toxicity information regarding additive 4 .

Only minimal amounts of Clam-Trol CT-1 are required for short treatment periods (6 to 24 hrs) to provide macrofouling control. The discharge of CT-1 concentrations of less than 1 mg/1 would not result in an environmental impact to the receiving stream or lake. In fact, even the most sensitive aquatic organisms would not be affected in either an acute or chronic sense beyond the mixing zone of the discharge stream. In addition, detoxified CT-1 remains neutralized so that it would not impact benthic organisms. Neutralized CT-1 actives would be further subject to biodegradation that would prevent any accumulation of these actives in the environment. The following toxicity information is available:

Appendix D: LC50 Values of Clam-Trol CT-1 (Neat formulation)

Appendix E: Detoxification Potential of Clam-Trol CT-1 with Clays and Other Materials To Fathead Minnows and Daphnia magna.

Appendix F: A 7-day Fathead Minnow Chronic Toxicity Test on the effect of Detoxified Clam-Trol CT-1 With Clays

Appendix G: Effect of Detoxified Clam-Trol CT-1 to a Benthic Organism: Chironomus, a midge larva.

Appendix H: A Long Term Study Using Fathead Minnows and Daphnia magna on the effect of Detoxified Clam-Trol CT-1

BETZ

Appendix I: Clam-Trol CT-1/Environmental Package Appendix J: Analytical Field Method for Clar Trol CT-1 Appendix K: MSDS

12

Larry A. Lyons Aquatic Toxicologist Laboratory Manager

Prepared by:\_\_\_\_

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Technical Paper 299

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# AMERICAN POWER CONFERENCE ILLINOIS INSTITUTE OF TECHNOLOGY CHICAGO, ILLINOIS APRIL 18–20, 1988

## EVALUATION OF A NEW MOLLUSCICIDE FOR ALLEVIATING MACROFOULING BY ASIATIC CLAMS

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#### EVALUATION OF A NEW MOLLUSCICIDE FOR ALLEVIATING MACROFOULING BY ASIATIC CLAMS

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#### ABSTRACT

Macrotouling by Asiatic clams impedes the efficiency, operation, and safety of power plants by plugging condenser tubes, threatens plant availability, jeopardizes safety-related water systems, and damages equipment. The current state-of-the-art control technology lacks an effective biocide for alleviating and preventing this seriis problem.

At TU Electric's Lake Hubbard station, the clam populations colonizing the intake bays caused chronic fouling of the main condenser tubes. The new molluscicide treatment program allowed the station to gain control of the macrotouling problem and then maintain control by exterminating juvenile Asiatic clams that recolonize the system. Seasonal molluscicide applications from June 1986 through October 1987 were shot fed to nonoperating intake bays. The performance of the molluscicide applications requiring only brief exposure periods has been evaluated with in situ biomonitoring methods.

#### INTRODUCTION

The cost of Aslatic clam macrofouling to the power industry is associated with reduced cooling efficiency and plant output by plugging condenser tubes, impaired and damaged circulating pumps and oil and hydrogen coolers, increased maintenance costs for equipment, and forced plant outages. These pests must often be physically removed from the systems they invade. EPRI has estimated that the loss of plant availability could cost \$500,000/day for a typical 600-MW coal unit, and the loss of 1% efficiency of a typical 600-MW coal unit exceeds 1 million dollars per year (1).

The threat to safety-related and service water systems is another major problem. Following the Arkansas Nuclear One forced outage, the 1981 NRC bulletin to all nuclear plant licensees recommended the implementation of a monitoring program for determining the severity of Asiatic clam fouling. It also recommended the establishment of preventative control measures for all safety-related components (2).

Attempts to control the proliferation, and thus the fouling ability, of the Asiatic clam have focused on physical and mechanical methods or the use of oxidizing biocides. The use of screens and strainers or physical removal measures (such as dredging and vacuuming operations) do not prevent the growth and proliferation of the clam, but only provide temporary relief from advanced fouling conditions. Oxidizing biocides, (e.g., chlorine or bromine) require weeks of continuous, uninterrupted applications to achieve efficacy (3). When continuous chlorination is permitted, the effect on corrosion, especially of copper alloys, is a major concern. Because Asiatic clams have chemoreceptors that detect low concentrations of oxidizing biocides, they can avoid contact by clamming-up for extended periods.

Alternative chemical control agents are either ineffective in short application periods, present an unacceptably high environmental risk, or cannot easily be detoxified before discharge (1, 4, 5).

This paper describes the successful application of a new molluscicide that is considerably more effective on the target organisms than chlorine and which can be conveniently applied to intake bays.

#### BIOLOGY OF THE ASIATIC CLAM

Asiatic clams, often referred to by their scientific name "Corbicula", are bivalve mollusks that thrive in fresh water environments. This extremely hardy species lives in a wide range of freshwater habitats throughout most of the United States. It can even prosper in moderately pol-

luted waters. The increased ambient water temperatures surrounding a power plant further enhances the proliferation and establishment of Aslatic clam populations.

Asiatic clams colonize in dense populations: 1000 to 10,000 clams per square yard are common. The clams are filter teeders that siphon in algae and bacteria from the water. Their natural productors are fish and crayfish. A plant's cooling system offers an ideal clam environment—It is free of predators and provides a continuous supply of food.

An Asiatic clam reaches sexual maturity when it is about 6 months old (14 in. In size). Each adult is capable of self-fertilization and can release many thousands of veliger larvae during the spawning seasons from Spring through the Fall.

Juvenile clams (less than 14 in. in size) and larvae are small enough to pass through cooling system intake screens. Once inside, they settle out primarily in low flow areas. They attain adult size within a few months and are then transported further into the cooling system. It is the transport of adult sized clams further into the cooling system that causes the chronic fouling problems that threaten the safety, operation, performance, and systems availability of power plants.

#### DEVELOPMENT OF A NEW MOLLUSCICIDE

The new molluscicide, called Clam-Trol CT-1 (patent pending), is effective against all life stages of the Asiatic clam, using short exposure periods of relatively low concentration. Clam-Trol CT-1 is an aqueous based formulation containing two cationic surfactants, alkyldimethylbenzylammonium chloride and dodecylguanidine hydrochloride.

This new molluscicide presents a unique advancement in the art of macrofouling control by having the capability of killing adult as well as juvenile Asiatio clams in cooling sytems using feasible, cost-effective treatment regimens. When applied, the material remains substantially undetected by the clam, which siphons in a lethal dosage during an exposure period of approximately 24 to 48 hr (depending on concentration and water temperature). A delayed mortality response occurs following the brief exposure period. Since the clam requires several months to a year to grow a shell of fouling size, periodic applications following peak spawning periods are sufficient to prevent clam fouling. Studies have shown that once the molluscicide actives are adsorbed by substrates (including sediments, suspended solids, and even the surfaces of cooling systems), they no longer exhibit toxicity to nontarget organisms (6). The molluscicide can also be actively detoxified with certain clays or other inert materials. If necessary.

#### APPLICATION EXPERIENCE

Although TU Electric's Lake Hubbard Station is the first field application to nonoperating intake bays, the new molluscicide has been used in other Asiatic clam control applications (7-9). Examples of other types of applications include a seasonal preventative treatment program for the service and safety-related water systems of a nuclear facility; a combined microorganism and Asiatic clam fouling control program of the molluscicide coupled with chlorine; and plant-wide applications to a steel mill with a water system network containing miles of pipelines.

#### LAKE HUBBARD STATION

The Lake Hubbard station of TU Electric, a two-unit gasfired generating facility, has experienced chronic fouling and forced outages resulting from the pluggage of the main condenser tubes by Asiatic clams.

Lake Hubbard's intake bays measure 40  $\times$  11 ft with a high-water depth of 40 ft (see Figure 1). Unit 1 has two intake bays (1A and 1B), and Unit 2 has three intake bays (2A, 2B, and 2C).

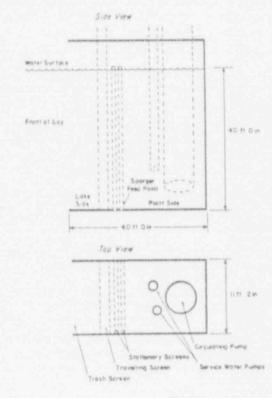


Figure 1.

Intake bay at TU Electric's Lake Hubbard Station. Aslatic clams colonize both the plant and lake sides of the five Intake bays. Each bay is equipped with one travelling screen and two stationary screens. Since these screens have a mesh size of 0.25 in., they do not restrict the infiltration of larval and juvenile clams. Even clams of 34 in. In size (about 6 months old) maneuver through the screens at all water depths (see Figure 2). These infiltrating juvenile clams then colonize and grow on the plant side of the Intake bays (see Figure 3). Adult clams that have attained the size of 1/2 to 3/4 in. are then transported to the main condensers and auxiliary coolers and plug the tubes. Previous clean-outs of the water boxes at the condensers have removed enough clams to fill two 55-gal drums.

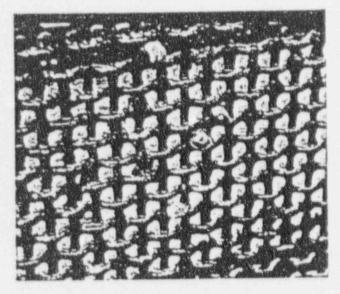


Figure 2. Juvenile Asiatic clams maneuvering through plant intake screens.

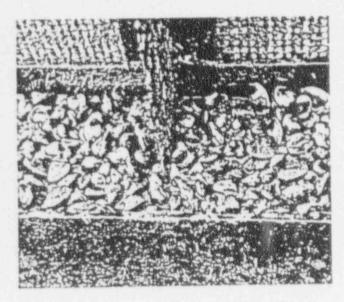


Figure 3. Clams colonizing plant side of intake screens.

Before this treatment, the only recourse for reducing the number of clams transported to the main condensers involved periodic mechanical clean-outs of the intake bays with the aid of scuba divers. These physical control measures only reduced the degree of pluggage by reducing the number of adult clams.

For these reasons. Clam-Trol CT-1 was applied to exterminate the juvenile clams that were recolonizing the Intake bays.

#### MOLLUSCICIDE APPLICATION METHODS

Lake Hubbard's Intake bays were inspected with the aid of a ponar dredge sampling device to estimate the density of the clam population residing in the bays and their size range. In many cases, mechanical clean-outs may be required prior to the initiation of molluscicide treatments in order to prevent a massive transport of dead clams further into the cooling system. At Lake Hubbard, the intake bays were cleaned out using divers.

The feed system was designed to maximize the dispersion of the molluscicide at the bottom of the intake bays. A sparge header (1-in, diameter and 10-ft long) was used that had a tee in the middle of the pipe for connecting a hose. The header was positioned at the bottom of the plant side of the secondary stationary screen.

A 50-gal stock solution of the molluscicide was prepared with lake water in a drum. The contents of this drum were then pumped to the header. Another 30 gal of lake water was also directed to the sparge header to assist in further diffusion of the molluscicide. Shot-fed dosages for the various applications were determined based upon the dilution of the stock solution by the total volume of water in the intake bay.

Following each treatment, the water from each intake bay was pumped with either the main circulating pump or service water pumps at a rate adjusted to assure sufficient dilution of the blocide at the discharge point. An analytical photometric method (10) was used for monitoring the discharge.

#### JUNE 1985 MOLLUSCICIDE APPLICATIONS

Two intake bays were treated in this application.

Bay 1B. The stationary screens in the intake bays at the Lake Hubbard Station are constructed with "I" beams, creating a 4-in, deep trough for the clams to colonize. The secondary stationary screen of bay 1B was cleared of all clams residing on the beams. Every other 3-ft beam was then reseeded with 75 clams ranging in age from 3 months to 3 years, and the stationary screen was low-

## TABLE 1: STATIONARY SCREEN "I" BEAM BIOMONITORING\*

		Cumulative % Mortality on the Following Days After Treatment						
Depth of Bay, ft	Ō	1	2	3	4	.c.5		
37	88	91	93	99	100	· ·		
31	0	36	63	77	81	85		
25	0	23	5	88	100			
19	0	0		5	11	15		
13	0	0	0	0	0	0		

\*June 1986 applications.

ered back into the bay. Bay 1B received four shot feed applications of 60 ppm each during a 48-hr treatment period. The clams were examined daily for 5 days following the treatment (see Table 1).

Bay 2B. The "I" beams of the secondary stationary screen of bay 2B were not cleared prior to the treatment but were allowed to retain the existing population. They were also examined during the post-treatment period. Only a qualitative examination was made, since the hundreds of live clams residing on the ledges were not counted prior to treatment. Bay 2B received two shot feed applications of 60 ppm each during a 24-hr treatment. During these examinations, dead clams were discarded and the remaining live clams were counted to provide percent mortality estimations (see Table 2).

Lake Side Monitoring. Following each treatment period, clams were collected from the lake side of each bay using a ponar dredge. The clams were transferred to aquaria for monitoring the mortality responses. The aquaria were replenished with fresh lake water two to three times daily during a 4-day post-treatment period.

#### TABLE 2: STATIONARY SCREEN "I" BEAM BIOMONITORING\*

Bay 2B: 24-hr Treatment Period/2 Shot Feed Applications (60 ppm Each)

	No. of Alive Clams Counted/ Estimated Cumulative % Mortality on the Following Days After Treatment				
Depth of Bay, ft	2	4			
37	12/>95	6/>95			
33	24/>90	15/>95			
28	280/30	115/>50			
21	400/<5	220/>25			

\*June 1986 applications.

These dredge samples were not monitored beyond 4 days, because of a significant clarm mortality from unknown causes that occurred in the control tank on the 5th day (see Table 3).

		Cumulative % Mortality on the Following Days After Treatment				
	1	2	3	4		
Control	0	0	0	2		
Bay 1B (Lake Side)	74	82	82	82		
Bay 2B (Lake Side) (Dredge Sample #1)	-	15	41	66		
Bay 2B (Lake Side) (Dredge Sample #2)	145	9	23	34		

TABLE 3: DREDGE SAMPLES OF CLAMS COLLECTED FROM LAKE SIDE OF BAYS\*

\*June 1986 applications.

In Vitro Monitoring. Treated water was collected from the 40-ft depth locations on the east and west sides of both bays and transferred to aquaria containing clams. The clams were collected from the intake bays prior to the treatments. Each aquarium received treated water 30 min and 3 hr following each shot feed application. Following the exposure period, each aquarium was replenished two to three times a day with fresh lake water. Dead clams were removed during the daily post-treatment examinations (see Table 4).

#### 1987 SEASONAL APPLICATIONS

In situ cages on the bottom of the bays were used for monitoring during the 1987 applications (see Figure 4). At specified intervals following the treatments, the clams retained within the cages were examined for mortality (see Tables 5-7). Ambient lake water temperatures for February, June, and October were 50, 75, and 68 \*F, respectively.

#### RESULTS OF APPLICATIONS

Molluscicide applications at the Lake Hubbard Station were assessed by biomonitoring methods. Clams were recorded as dead when the bivalve shell had gaped open. Occasionally, the viability of a clam was determined by gently prying open the bivalve shell slightly. A clam was judged to be alive if it clammed up again.

June 1986 Applications. Mortality responses of between 90 and 100% were observed for both the 24-hr treatment with two-dose applications (bay 2B), and the 48-hr treatment with four dose applications (bay 1B) (see Tables 1 and 2).

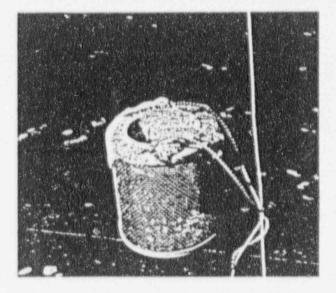


Figure 4. Cricket cages used for in situ biomonitoring.

A stratification of the molluscicide at the lower depths of the intake bays was observed, as exemplified by mortality responses ranging from 100% at the 37-It depth to 15% at the 19-It depth (see Table 1). This biomonitoring of the vertical molluscicide dispersion supports localizing the applications to the bottom of intake bays where Asiatic clams tend to colonize and grow. Even the clams that were recolonizing the lake sides of the intake bays were exterminated guite effectively (see Table 3).

The lower mortality responses recorded in Tables 3 and 4 were continuing when the monitoring was terminated

ay 1B: 48-hr Treatment	Period/4 Shot	Feed Appli	cations (60 pp	im Each)				
		Cumulative % Mc tality on the Following Days After Treatment						
	0	1	- 2	3	4			
Control	0	0	0	Q	3			
1B-Plant Side	6	95	98	100				
1B-Lake Side	12	66	100					

#### TABLE 4: IUNE 1986 APPLICATIONS/AQUARIA BIOMONITORING

Bay 2B: 24-hr Treatment Period/2 Shot Feed Applications (60 ppm Each)

		Cumulative % Mortality on the Following Days After Treatment				
	1	2	3	4		
2B-Plant Side	0	0	30	63		
2B-Lake Side	30	88	100			

because of unexplained clam mortality in the control tank 5 days after treatment.

February 1987 Applications. The colder water temperatures during this time of year resulted in a slower rate of mortality response. However, increasing the application period to 72 hr caused clarn kills of 98% to 100% on the plant side of the bay (see Table 5).

A slower kill rate was also observed in cold water applications at another facility (8). This may be attributed to reduced metabolic and siphoning activity by the clam during the winter months. June 1987 Applications. All three applications resulted in clam mortalities of 96% to 100% for the plant sides of the intake bays (see Table 6). Clam mortalities on the lake side of the intake bays ranged from 25% to 85%.

October 1987 Applications. A 100% mortality response was achieved on the plant side of the intake bay being monitored. No clarn mortalities were reported on the lake side (see Table 7). Further modifications or positioning of the sparge header may be required to increase the dispersion of molluscicide to the take side of the bays if extermination of the recolonizing clams is needed.

### TABLE 5: FEBRUARY 1987 APPLICATION RESULTS

		Cumulative % Mortality on the Following Days After Treatment					
	0	1	2	3	18		
1A-Plant Side (back of bay)	56	82	86	86	98		
1A-Plant Side (middle of bay)	32	46	50	76	106		
1A-Lake Side (front of screen)	2	6	6	6	6		

Bay 2A: 48-hr Treatment Period/4 Shot Feed Applications (60 ppm Each)

	Cumulative % Mortality on the Following Days After Treatment							
	0	1	2	3	4	18		
2A-Plant Side (back of bay)	0	24	26	30	32	46		
2A-Plant Side (middle of bay)	20	32	58	72	80	96		
2A-Lake Side (front of screen)	0	4	4	10	10	10		

Bay 1B: 24-hr Treatment Period/2 Shot Feed Applications (60 ppm Each)

	0	1	2	3	18	
1B-Plant Side (back of bay)	б	30	44	50	50	
1B-Lake Side (front of screen)	0	0	4	4	4	

## TABLE 6: JUNE 1987 APPLICATION RESULTS

		ulative % Mor wing Days At		
	1	2	3	5
2A-Piant Side	77	96	96	96
2A-Lake Side	0	0	25	25

Bay 2B: 48-hr Treatment Period/2 Shot Feed Applications (50 ppm Each)

		ilative % Mor ving Days Af	tality on the ter Treatment		
	1	2	3	5	
28-Plant Side	11	43	91	97	
28-Lake Side	59	85	85	85	

Bay 2C: 48-hr Treatment Period/1 Shot Feed Application (100 ppm)

Cumulative % Mortality on the

	Follo	Following Days After Treatment				
	1	2	3	5		
2C-Plant Side	96	100				
2C-Lake Side	8	4.4	52	52		

## TABLE 7: OCTOE IR 1987 APPLICATION RESULTS

Bay 2C: 48-hr Treatment Period/1 Shot Feed Application (100 ppm)

Cumulative % Mortality on the

Fol	lowi	ng l	Days	AI	ter	reatr	ment

		1	2	3
2C-Plant	Side	57	98	100
2C-Lake	Side	0	0	0

#### CONCLUSIONS

The new molluscicide, Clam-Trol CT-1, is extremely eftective against all life stages of the Asiatic clam with only brief treatment periods of 24 to 48 hr. It can be easi applied by shot feed or continuous feed (depending on the system to be tre\_ted) and, if necessary, detoxified prior to discharge.

For optimum results, the Asiatic clam control program consists of three basic steps for eliminating clam populations and preventing recolonization.

Step 1. Adult clams in the cooling system are physically removed by dredging or vacuuming operations. This stops the mass transport of clams and relic shells further into the system and, consequently, prevents tube pluggage.

- Step 2. Molluscicide is applied using appropriate methods to assure good distribution to the areas of colonization. Vigilance to prevent the further transport of adult clams that were not removed during the cleanout operations is required.
- Step 3. Seasonal applications (2 to 4 times per year) are scheduled to exterminate larvae and juvenile clams that will be recolonizing the system.

ALLake Hubbard, mortality responses of 90-100% were consistently observed for each of the four seasonal applications to the plant side of the intake bays. The molluscicide was conveniently shot fed and diffused to the bottom of the intake bays with a sparge pipe. The easy-touse biomonitoring methods that were used for evaluating treatment effectiveness can also be used for optimizing the application. If the molluscicide is fed during the winter months, a longer application period may be required to compensate for reduced metabolic and siphoning activity in cold water. Regulatory requirements are met by moditying discharge procedures.

Seasonal applications of the new molluscicide at Lake

Hubbard proved to be a good economic alternative for Asiatic clam control. The treatment program was effective in exterminating juvenile and larval clams and preventing the reinfestation of adult clams in the intake bays. The most significant benefit to the Lake Hubbard Station is the reduced tube plur jage in the main condenser and auxiliary coolers. This not only improves cooling efficiency, but also minimities microfouling and sedimentation. Multenance activities, such as blowing and rodding of tubes, have also been greatly reduced. Vacuuming of intake bays is no longer necessary. The control of Asiatic clam macrofouling has eliminated forced unit outages due to clams at the Lake Hubbard station.

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Technical Paper 320

EPRI Service Water System Reliability Improvement Seminar

## ASIATIC CLAM CONTROL EXPERIENCE AT PEACH BOTTOM ATOMIC POWER STATION

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## ASIATIC CLAM CONTROL EXPERIENCE AT PEACH BOTTOM ATOMIC POWER STATION

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#### ABSTRACT

A preventive treatment program effectively controlled Aslatic clams in the service water and safety related cooling systems at the Peach Bottom Atomic Power Station of Philadelphia Electric Company. The molluscicide used, a nonoxidizing biocide, provides 100% efficacy after a short exposure period and is more environmentally attractive than traditional oxidizing biocides. This paper details the Aslatic clam control program at Peach Bottom and describes application experiences. The spawning characteristics of the Aslatic clam in the plant makeup waters with respect to time and temperature, as well as molluscicide treatment levels and feed duration, are also reviewed.

#### INTRODUCTION

Asiatic clam macrofouling is estimated to cost U.S. Industry more than \$1 billion annually. These costs are related to flow restrictions, reduced cooling efficiency, maintenance expenses, replacement of damaged equipment, and forced outages.<sup>1</sup> The vulnerability of fire-protection systems and safety-related systems in nuclear-fueled generation stations is of special concern.

Early attempts to control the proliferation, and thus the fouling ability, of the Asiatic clarn were focused on physical and mechanical methods or the use of oxidizing biocides. These control measures, however, were proven to be largely ineffective. The use of screens and strainers or physical removal measures (such as dredging and vacuuming operations) provide only temporary relief from advanced fouling conditions. They do not prevent the growth and proliferation of the microscopic larval and juvenile clams. Oxidizing blocides (e.g., chlorine or bromine) require weeks of continuous, uninterrupted applications to achieve efficacy.<sup>2</sup> When continuous chlorination is permitted, the effect on corrosion, especially of copper alloys, is a major concern. Because the chemoreceptors of Asiatic clams detect low concentrations of oxidizing blocides, the clams avoid contact by "clamming-up" for extended periods.<sup>3</sup> Advances in treatment technology over the past few years allow this macrofouling problem to be addressed using a nonoxidizing blocide. The Asiatic clams do not sense the nonoxidizing material in the water and siphon in a lethal dose during an application period.

### APPLICATION EXPERIENCE AT PEACH BOTTOM

The Peach Bottom Atomic Power Station is a two-unit boiling water reactor with once-through cooling water systems. Located on the Susquehanna River in southerm Pennsylvania, the station found Asiatic clams in both the cooling water intake bays and discharge canal. Due to environmental discharge limitations, extended low-level continuous chlorination was not possible at Peach Bottom.

In the Spring of 1987, the application of an environmentally acceptable molluscicide that provides 100% mortality on adult Aslatic clarns within a 24-hour exposure period was recommended to Philadelphia Electric. The proposed benefits of the new molluscicide were: relatively small, economical dosages were required, the product was easy to apply, and it was noncorrosive to system metallurgy.

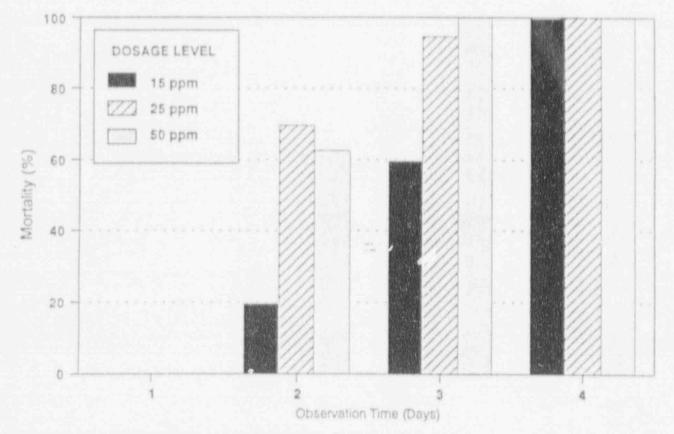
The product (Betz\* Clam-Trol\* CT-1) is registered by the U.S. EPA for use against mollusks in once-through systems, recirculating cooling systems, influent systems, and auxiliary water and waste systems (including intake bays and fire-protection systems). The active ingredients in the product are a quatemary amine (QUAT) and dodecylguanidine (DGH) in an aqueous solvent system. The product contains no heavy metals or EPA priority pollutants. Both actives are cationically charged surfactants that are readily adsorbed by naturally occurring materials, such as clay, suspended solids, humic acids, and sediment. Once adsorbed, the actives are not toxic to aquatic species.<sup>4</sup>

Based on the success of laboratory evaluations performed by RMC Environmental Services (see Figure 1) and projected savings compared to hypochlorite injection, permission was obtained from the Pennsylvania Department of Environmental Regulations (PADER) to apply the molluscicide to the service water, high-pressure service water (HPSW), emergency service water, and fire protection systems of Units 2 and 3 at the Peach Bottom Atomic Power Station.

#### Cold Water

The molluscicide was first applied in December 1987 to the high-pressure service water systems. Clam mortality was monitored using several hundred adult clams from the Susquehanna Piver that were graded in size in a multichambered aquarlum. Product concentration was monitored throughout the 48-hour application using a colorimetric test procedure. The product was applied to the inlet of the HPSW system at a concentration of 25 ppm. Free product residual at the discharge of the HPSW system was 17.5 ± 1.5 mg/L. Free product concentration to the Susquehanna River at the outfall was below detection limits (less than 1.0 mg/L) after reaction with the solids in the circulating water dilution flow. This circulating water flow provided a dilution factor well below the LC50's of the molluscicide to aquatic organisms.

During the application, two sample populations of Corbicula were placed in aquaria and exposed for 24 and 48 hr, respectively, to free product residual intreated water obtained from the HPSW system. This provided additional data on the required exposure period under low temperature conditions (5-7 °C). The aquaria were placed in an insulated blobox through which water was circulated to maintain clams at ambient water temperature. The treated water was replaced hourly for





the first 2 hr of injection and then at 4-hr intervals for the duration of the 48-hr exposure. Following the 48-hr exposure, the clams were moved off-site to a nearby laboratory and maintained at 5-7 °C along with the control population. Whereas the control population continued to siphon normally, both treated populations ceased all siphoning activities after exposure. A portion of the control group, 24-hr exposure group, and 48-hr exposure group was sacrificed at 1, 11, 16, 23, 27, 30, and 37 days following the initial exposure, and the pill tissues were examined under a microscope for cillia beating. The results (Figure 2) show that 100% mortality was achieved in both the 24-hr and 48-hr exposure groups, while 0% mortality was observed in the control population. The retardation of the latent r ortality response under cold water (5 °C) conditions was considered particularly significant. Another significant finding of Philadelphia Electric's clam control program is that clams in the Susqueharina River spawn from mid-May through late fall and that during the winter months, juvenile and adult Asiatic clams survive for weeks in harsh winter water temperature (0-1 °C). Brooding larvae were found in adults in December 1987 at ambient water temperatures approaching 5 °C (see Figure 3). This finding is troublesome for the industry, since it suggests that the species is beginning to adapt to colder climates once thought to be a barrier to survival In the northern United States.

This adaptation to cold weather also presents a difficult problem from a treatment standpoint. Based on observations of clams evaluated by RMC Environmental Services, Corbicula exposed to water at less than 2 °C rarely siphon compared to those maintained at 5 to 6 °C. This limited siphoning activity complicates the treatment program and extends the latent efficacy period, probably beyond that seen in Figure 2 at 5-7 °C.

### Warm Water

Based on these findings, further treatments to the PBAPS service water systems were postponed until the summer of 1988. In August of 1988, molluscicide was applied for a 24-hr period to the Unit 2 HPSW system. Twenty-five parts per million of the molluscicide was ted at amblent water temperatures ranging from 24 to 29.5 °C. Mean molluscicide concentration throughout the treated systems during the exposure period was 19.8  $\pm$  1.4 ppm. Monitoring was conducted as described earlier utilizing the biobox, and *Corbicula* were exposed for 12 and 24 hr. At the end of the exposure periods, test clams were again transported to holding facilities at a nearby laboratory and monitored for latent mortality. Water temperatures in the holding facilities ranged from 23 to 24 °C throughout the mortality observation period.

The latent mortality of control and test clams exposed to the Clam-Trol CT-1 molluscicide for 12 and 24 hr at

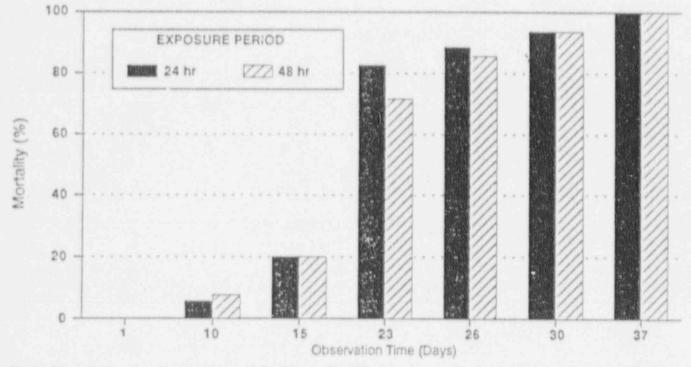


Figure 2: Latent mortality response of Corbicula: PBAPS (Dec 8-10, 1987), HPSW loop 3B, water temperature 5-7 °C.

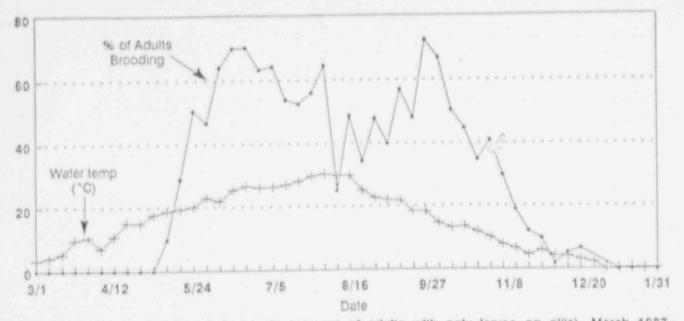


Figure 3: Spawning activity of Corbicula (percent of adults with only larvae on gills), March 1987-January 1988.

24-29.5 °C is shown in Figure 4. Test clams in both the 12 and 24 hr tests experienced 100% mortality within 76 and 88 hr, respectively. The control clams experienced no mortality.

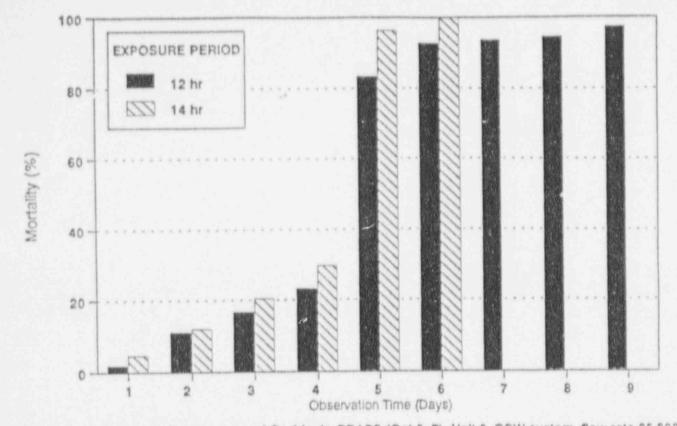
Two additional applications took place in October of

1988. Treatment and monitoring techniques were

conducted in the same manner as described above. The Unit 2 General Service Water (GSW) system was treated when water temperatures were approximately 18 °C, while the Emergency Service Water (ESW) system was treated a week later with ambient water temperatures between 15 and 16 °C. As shown in Figures 5 and 6, the

100 EXPOSURE PERIOD 5 24 hr 12 hr 80 ----Mortality (%) 60 40 4 20 0 72 88 64 48 24 Observation Time (hr)





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Figure 5: Latent mortality response of Corbicula: PBAPS (Oct 6-7), Unit 2, GSW system, flow rate 25,800 gpm, water temperature 18 °C.

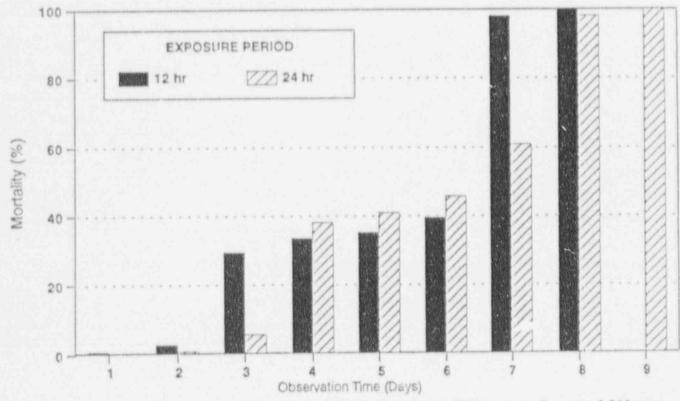


Figure 6: Latent mortality response of Corbicula: PBAPS (Oct 13-14), ESW system, flow rate 3,300 gpm, water temperature 15-16 °C.

time to achieve 100% mortality increased with lowering temperature, as expected based on earlier observations. Figure 7 summarizes the time to achieve 100% mortality as a function of water temperature. The increased time to achieve mortality is directly related to the decreased siphoning activity of the Asiatic clam while in a cold water environment.

The resident fish population was monitored during the cold and warm water injections. No visible effect was noted on the fish population.

#### CONCLUSIONS

The application of a nonoxidizing blocide st Peach Bottom resulted in 100% mortality in Aslatic clams with a 24-hr exposure period at temperatures as low as 5 °C. Latent mortality of the clams increased with lower ambient water temperatures.

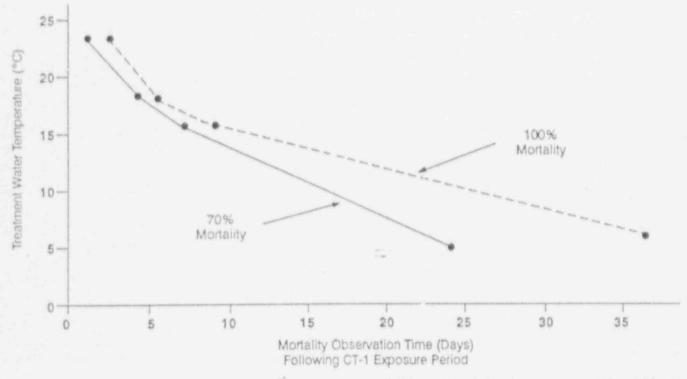
When water temperatures were greater than 15 °C, both 12 and 24 hr applications of molluscicide at similar concentrations were equally effective in killing clams. Further testing is being conducted to confirm these results and could lead to shorter injection periods during the summer months. The advantages of a shorter injection period are both economical (reduced chemical and feeding costs) and operational (system components can be tested and returned to operation sooner).

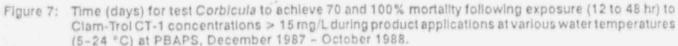
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Future plans are to evaluate the installation of a permanent feed system for the molluscicide at Peach Bottom Atomic Power Station. This will allow for short periodic injections of the product on an intermittent basis throughout the year to control the station Asiatic clam population.

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Electric Light & Power November 1987

# Molluscicide controls Asiatic clam problems

R.M. Post Betz Industrial and L.A. Lyons Betz Laboratories

A new cost-effective chemical treatment that can be used at both fossilfueled and nuclear power plants uppears to offer an exciting new weapon for use in the battle against the Asiatic clam.

Asiatic clam fouling is estimated to cost U.S. industry more than \$1 billion annually. These costs are related to power outages or plant shutdowns, reduced operating efficiencies, maintenance expense, replacement of equipment and other costs associated with controlling this pest. The vulnerability of safety-related systems, including fire sprinkler equipment, also is a major concern to industrial managements.

#### Mechanical/ Physical Control

Screens and strainers c. t prevent microscopic larval ar venile clams from infesting cooling statements. Other mechanical methods, such as wire mesh across the face of tube sheets or plastic strainers in tube inlets, still require the physical removal of accumulated clams, shells and entrapped debris.

Physical control measures consist primarily of dredging and vacuuming adult clams from accessible low-velocity areas, where clams are prone to colonize. This operation often requires the use of divers. Outages or reduced load operations are required to allow water boxes, service water heat exchangers and piping to be cleaned out.

Moreover, mechanical or physical control methods do not prevent fouling. They merely provide a means of dealing with advanced fouling conditions.

#### Chemical control

In order to reduce the severity of clam infestations with chlorine or other oxidizing biocides, such as bromine and chlorine dioxide, continuous, un-

interrupted applications are required over several weeks. But Asiato clams have chemoreceptors that can detect very low concentrations of axidizing biocides. When they sense the presence of these materials, the clam avoids contact by "clamming up," closing its shell and remaining that way for extended periods. Thus it is believed that axidizing biocides cause clam mortality by asphyxiation, rather than by direct toxicity.

Since clams will resume siphoning as soon as the chlorine residual disappears, any interruption in chemical feed for maintenance or repair of the chlorination system will result in ineffectual control of the clam population. In addition, continuous chlorination requires large inventories of chlorine gas, which not only is expensive, but also is the subject of growing insurance and safety concern.

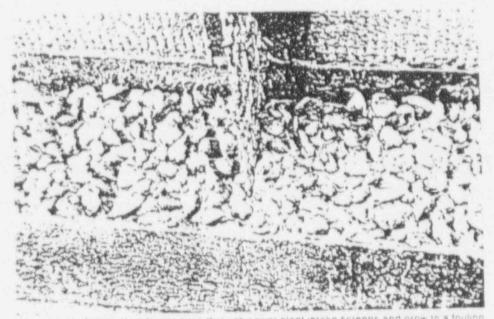
Use of liquid sodium hypochlorite

bleach alleviates the safety concernbut costs several times more than gaseous chlorine. Utilities also are under increasing environmental presures to reduced their discharge of total residual chlorine. Continuous chlorination dechlorination would enable complaince, but again at increased expense.

#### Recent developments

The ideal chemical control agent would provide effective extermination of Asicatic clams with short application periods within the plant and could be rendered non-toxic before its discharge. Betz Laboratories recently has introduced a molluse cole that closely matches these requirements

The new molluscicide exterminates all life stages of the Asiatic clam with a single short application of 12 to 48 hours, depending on concentration and temperature. Treatment pro-



Microscopic Asiatic clam larvae pass through power plant intake screens and grow to a fouling size downstream. These fresh water clams demonstrate the futility of screening devices.

grams employing the new molluscicide range from simple extermination applications at intake structures and other in-plant colonization areas all the way to large-scale plant-wide applications involving multiple reservoirs and miles of pipe. The frequency of application is based on the clams' seasonal spawning activities and the vulnerability of the system to clam infestation.

After the initial application and removal of large shells, periodic applications are made to exterminate larvae and juvenile (less than Vs-in, dia.) clams. This prevents shell growth to a fouling-size, which would occur in just a few months.

The liquid molluscicide is dispensed easily from portable 300-gal, bulk

containers, using standard metering pumps. Since the containe:s are returned when empty. costly on-site storage and handling facilities are not required.

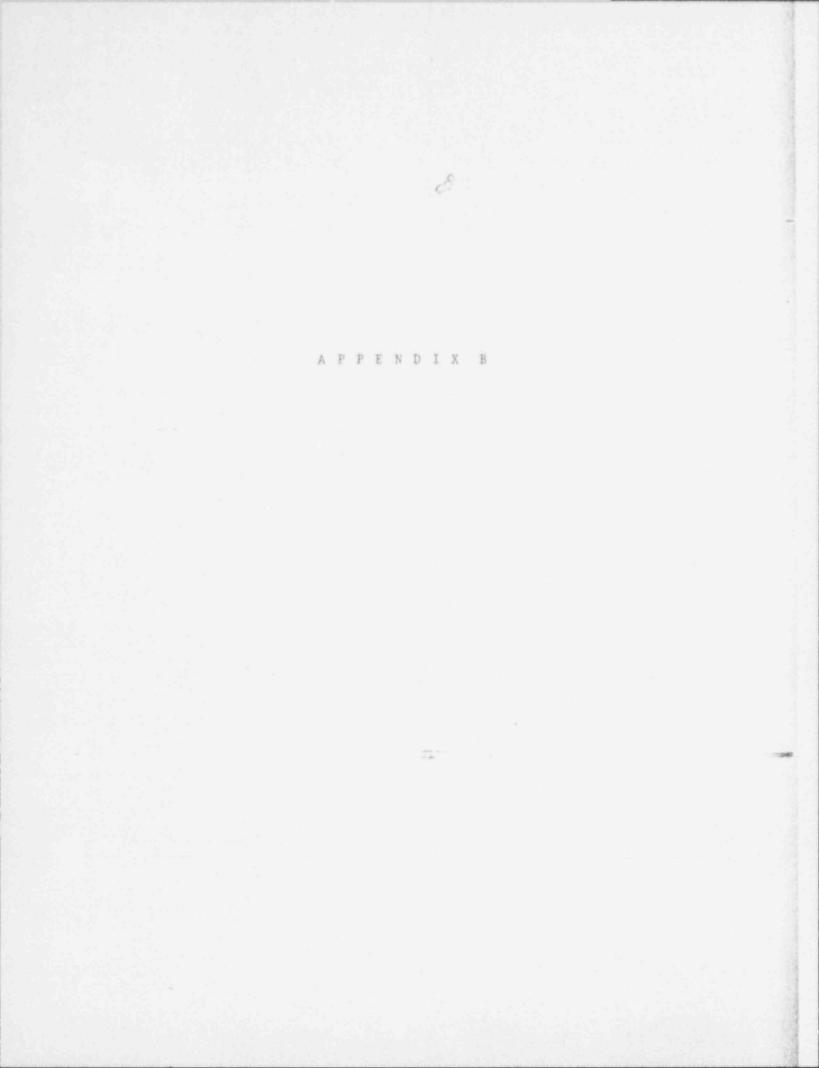
#### Environmental considerations

In contrast to chlorine or other oxidizing biocides, the new molluscicide involves short application periods and small product requirements. These result in only minimal chemical additions to the environment. Moreover, the chemical is rapidly neutralized or detoxified. The active constituents are short-lived because they can be adsorbed onto a variety of substrates, including suspended solids, sediments, and even the surfaces of cooling systems. Studies have shown that once the organic active materials are adsorbed, the molluscicide no longer exhibits toxicity with regard to fish.

Molluscicide applications are tailored to make the best use of these passive absorptive properties. If required, the detoxification process can be accelerated by the addition of specific detoxification agents. An analytical method using prepackaged reagents and a photometer also is available for monitoring product concentrations.

The material has been registered with the EPA by Betz Laboratories for use against Asiatic clams in oncethrough and recirculating cooling systems, influent systems and fireprotection systems.









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Society of Environmental Toxicology and Chemistry (SETAG); Presented at foronto, Canada Meeting October 28 - November 2, 1989

> FOULING CONTROL FOTENTIAL FOR ZEERA MUSSELS WITH CLAM-TROL CT-1, A MOLLUSCICIDE. L. A. Lyons, D. P. Davis, J. C. Petrille, M. W. Werner, Betz Laboratories, Inc., Trevose, PA; William Kovalak, Detroit Edison, Detroit, MI.

The Zebra mussel, Dreissena polymorpha, is an European mollusk that has invaded the Great Lakes within the past few years. This new pest is becoming well adapted and already imposing major fouling concerns by attaching to the bottoms of boats, growing within potable water supply intake conduits, and threatening the operations of power plants. An estimation of 2000 mussels/mª within the intake bays of a cooling system have been reported at a power plant near Detroit. Chlorination practices for controlling this mollusk infestation to cooling systems cannot be accomplished without continuous application for several weeks.

A new molluscicide, Clam-Trol CT-1, that is providing state-of-the-art control for Asiatic clam fouling to power plants and industrial facilities, has also demonstrated its effectiveness toward the Zebra mussel in laboratory studies. Efficacy determinations for Clam-Trol CT-1 concentrations from 5 mg/1 to 15 mg/1 for exposure periods of 6 hrs. to 24 hrs. have been evaluated at 10°, 15°, and 20°C. Mortality responses were shown to be dependent upon dosage, exposure period and temperature.

Update: A recent inspection (Sept. 1989) at a Detroit Idison power plant estimated 600,000 mussel/m2 were attached to all surface areas within the intake bays of the cooling system.

Note: Clam-trol CT-1 is a formulation containing 13% active ingredients. Effective feed concentrations of 5 mg/1 to 15 mg/1 as Clam-trol CT-1 would represent total active concentrations of 0.65 mg/1 to 1.95 mg/1.

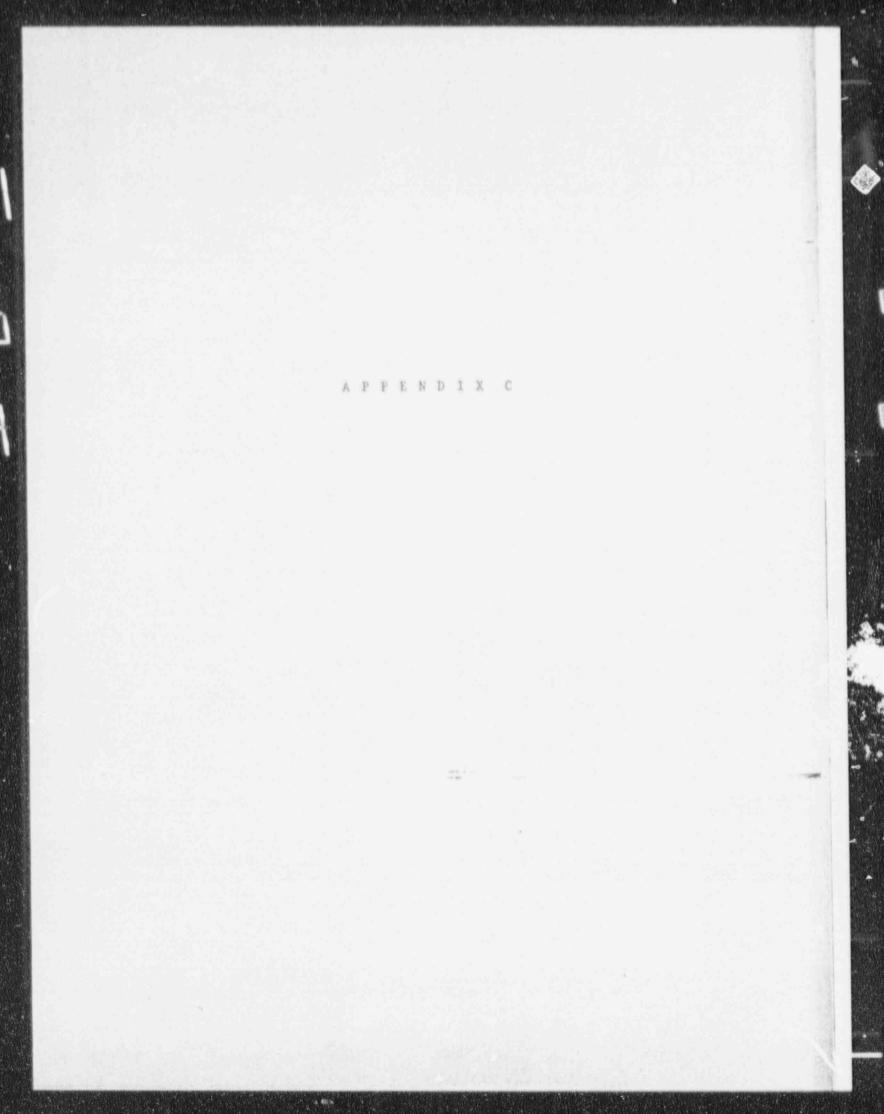
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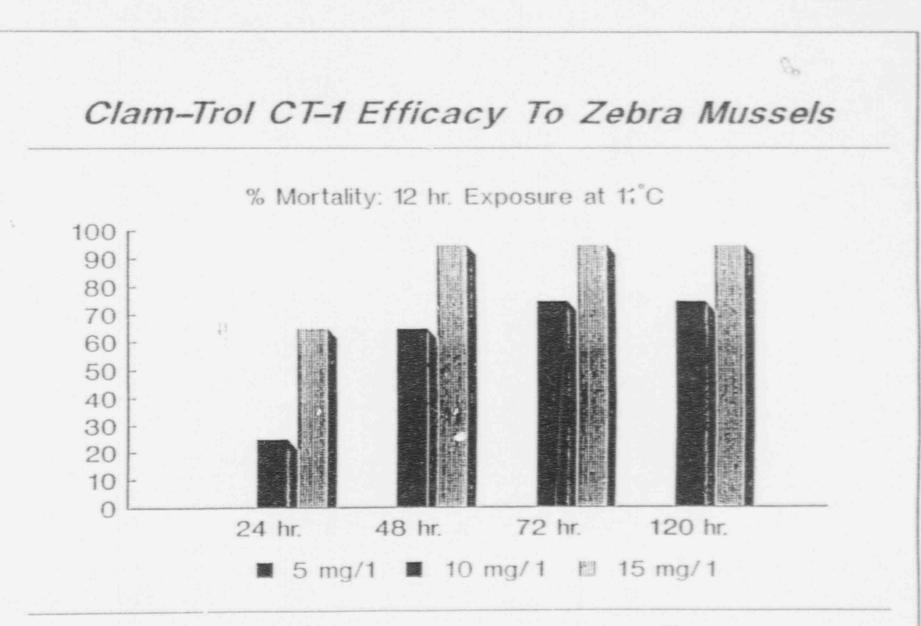
# Clam-Trol CT-1:

# A Molluscicide That Controls Fouling by Zebra Mussels and Asiatic Clams

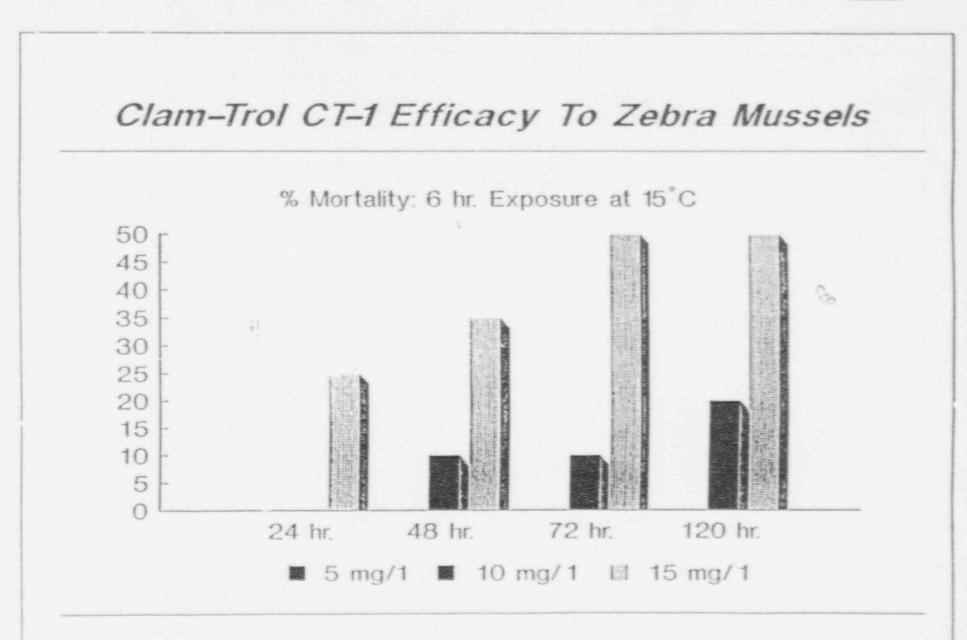
concentrations of 5 mg/1 to 15 mg/1 as Clam-trol GT-1 would represent total of two concentrations Note: Clam-Trol CT-1 is a formulation containing 112 active ingredients. Effective feed of 0.65 mg/1 to 1.95 mg/1



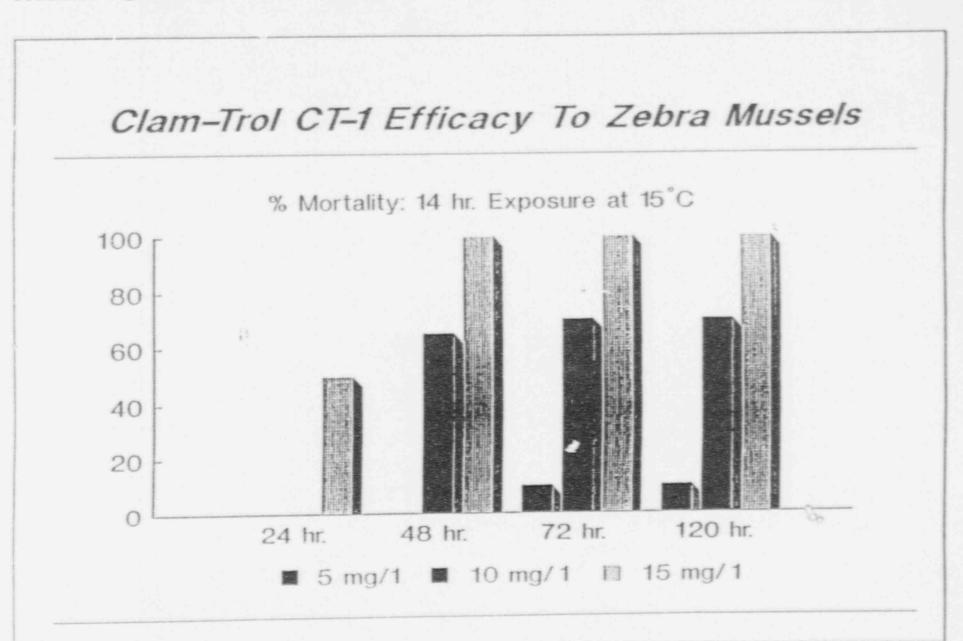
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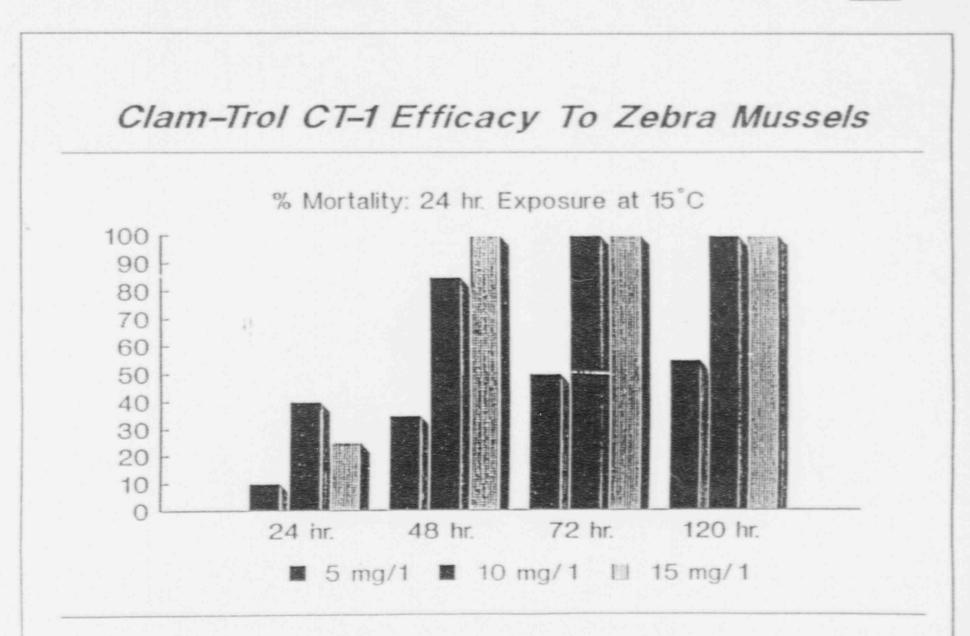
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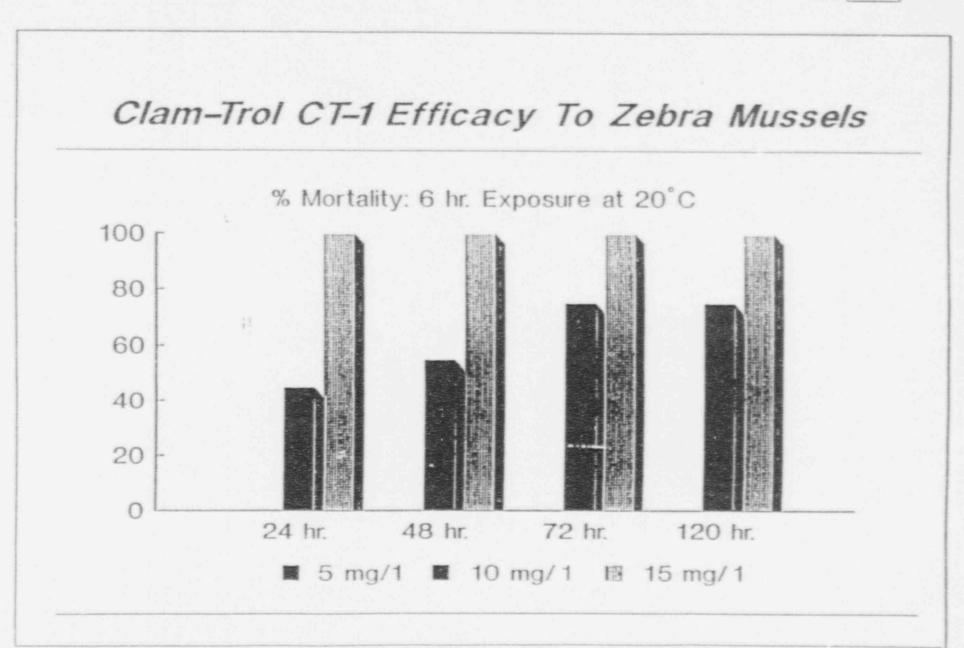
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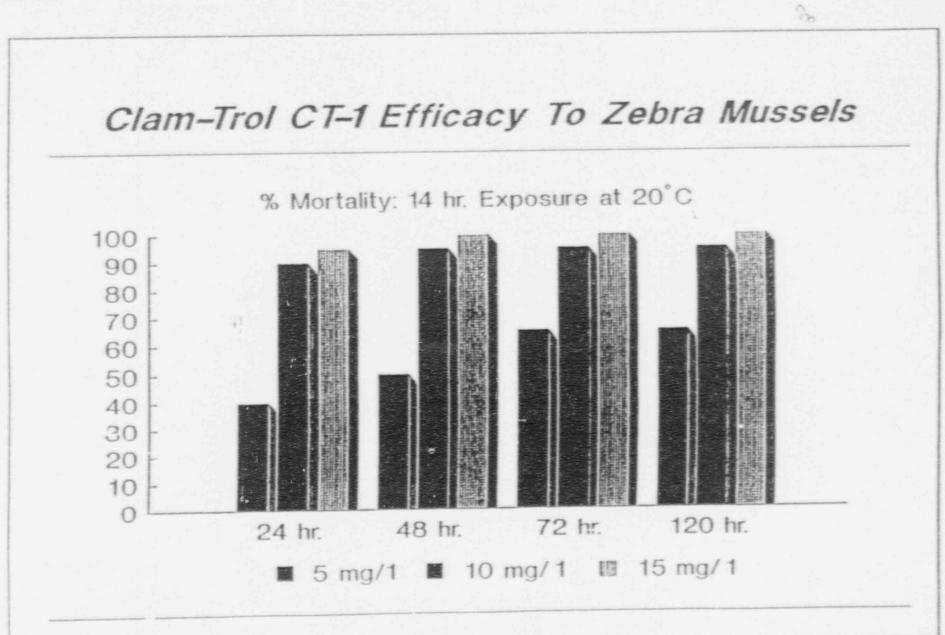


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Technical Paper 325



American Power Conference Illinois institute of Technology April 1, 1990

# New Treatment Employing a Molluscicide for Macrofouling Control of Zebra Mussels in Cooling Systems

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#### NEW TREATMENT EMPLOYING A MOLLUSCICIDE FOR MACROFOULING CONTROL OF ZEBRA MUSSELS IN COOLING SYSTEMS

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#### ABSTRACT

The Zebra mussel is a European mollusk that has intested the Great Lakes within the past few years. This new pest is extremely prolific and aggressively attaches to all types of surfaces. Power plants situated around Lake Erie and Lake St. Clair are experiencing extensive mussel macrofouling. Incidences of macrofouling include colonies of more than 500,000 mussels per square meter, these mussels completely cover all surface areas of intake bays, plug chiller units and main condenser tubes, and grow within service-related cooling pipes. There is an obvious danger of forced outages if preventative measures are not taken.

A nonoxidizing molluscicide, Clam-Trol® CT-1, which is providing state-of-the-art control for Asiatic clam fouling in power plants, has also demonstrated effectiveness in controlling Zebra mussels. The results of efficacy determinations from laboratory studies for ClamTrol CT-1 at concentrations from 5 mg/L to 15 mg/L, for exposure periods of 6 to 24 hr, and at water temperatures of 11 °C, 15 °C, and 20 °C are provided. The optimum CT-1 application for mussel fouling control will be dependent upon dosage, exposure period, and water temperature. It is anticipated that many systems will require seasonal applications (2 to 4 times/year) based upon growth rate, spawning season, and extent of setting by mussel larvae. Two power plants near Detroit, Michigan received the first CT-1 applications during the fail/winter of 1989. The J. R. Whiting Power Plant, a 3-unit (350 MW, coal-fired facility, received 12-hr applications to each main circulating and service water system. The Chrico Fermi II Nuclear Power Plant, a 1-unit (1100 MW) facility, received a 15-hr CT-1 application to the service water system. The performance of these applications was biomonitored using flow-through bioboxes. Mortality responses were correlated with dosage and water temperature. Recommendations for optimizing treatment programs based upon seasonal ambient water temperatures and the degree of mussel infestation are provided.

#### INTRODUCTION

Zebra mussels are estimated to cost the Great Lakes region 5 billion dollars between 1990 and 2000 (1). Zebra mussels will adversely impact commercial fisheries, recreational activities, potable water suppliers, and industry. They will also significantly uter the ecosystems of these takes. Zebra mussels are expected to spread throughout the Great Lakes and to many rivers and takes of North America within the next 5 to 10 years.

Juvenile mussels or veliger larvae were probably transported to the Great Lakes In 1986 via the ballast water in a ship originating from a European treshwater port. Zebra mussels were first found in Lake St. Clair in 1988. Presently, Zebra mussels are found throughout Lake Erie; the most extensive populations are in the Western Basin. Scattered populations of Zebra mussels have been reported in Lake Ontario and a few mussels have also been found in Lake Michigan's Green Bay.

The prolific and rapid growth of Zebra mussel populations attest to the need for a monitoring program at raw water intakes. These monitoring programs provide surveillance for mussel intestation and determine the degree of colonization and fouling within a cooling system. This rapid colonization has been exemplified at the Detroit Edison Company's Monroe Power Plant located on the Western Basin of Lake Erie. The densities of Zebra mussels found in the intake canal at the Monroe station have increased exponentially from 50 mussels/m<sup>2</sup> in the fall of 1988 to greater than 700,000 mussels/m<sup>2</sup> in the fall of 1989 (2).

This macrofouling pest aggressively attaches to all types of hard substrates, including cement walls, screens and trash racks, pump housings, pipes of assorted metallurgy, plastic, rubber, and so forth. They tend to form large clusters by attaching to each other (see Figure 1). The formation of clusters of mussels near or within the intake structure of cooling systems threatens circulation pump operation and increases the potential of a forced outage. In addition, in the veliger larval stage, this mussel will pass through all intake screens and in-line basket screens and will settle within the cooling system. The juvenile mussels can encrust the entire surface areas of pipes. Encrustation can impede or completely restrict the flow of water through these pipes. The smaller diameter pipes within service water and safety related systems are particularly vulnerable.

#### Biology of the Zebra Mussel

The reproductive capacity and life history characteristics of the Zebra mussel, *Dreissena polymorpha*, explain the successful invasion and rapid colonization to aquatic environments. Reproduction of the Zebra mussels is highly prolific with a spawning season extending from the spring, when water temperatures rise above 12 °C to 15 °C, to October. Zebra mussels are dioecious (sepa-



Figure 1: Cluster of Zebra Mussels Attached to a Native Mollusk Shell

rate sexes) and mature sexually within one year. Fertilization is external and females can release approximately 30,000 to 40,000 eggs per year. The fertilized eggs develop to a planktonic veliger larval stage; the larval stage is microscopic (0.1 to 0.3 mm). The planktonic veliger stage lasts for 8 to 15 days during which they are dispersed by the water currents of lakes and rivers. In Lake Erie during 1989, veligers numbered from 40,000 veligers/m<sup>3</sup> in early summer to 500,000 veligers/m<sup>3</sup> in late summer (3).

The planktonic veligers develop to a post-veliger or juvenile mussel stage to begin the sedantary life. They secrete byssal threads for attaching to hard surfaces. Attachment by the byssal threads is quite tenacious and able to withstand water velocities of 3 to 5 ft/sec. Zebra mussels tend to be quite gregarious; they colonize in massive clusters and mats.

#### Control Methods: European Experience

Control measures employed in Europe for fouling control of Zebra mussels has involved mechanical/physical methods (4,7,9) and the use of oxidizing chemicals (4,5,6,8).

The various physical/mechanical control methods include: clean-outs, piping replacement, screening and straining, thermal backflushing, ultrasonic vibration, and electrical shock. Clean-outs for the removal of mussels and the replacement of piping requires scheduled plant outages. Although screens and strainers do not prevent the entrainment of juvenile or larval veligers into the cooling systems, they are necessary to prevent the transport of adult mussels or clusters of mussels further into a cooling system. Thermal backflushing of heated condenser water can provide fouling control for selected areas of a cooling system, usually intake bays. For those facilities having thermal treatment capabilities, a 15 - 60 min application at 40 °C will effectively control mussel infestations. Ultrasonic vibration and electrical shock have also been attempted in Europe with varying degrees of success.

Chlorination is the most common chemical control for Zebra mussel fouling. Continuous chlorination for 2 – 3 weeks is required to achieve efficacy. Intermittent chlorination programs, that feed a few hours each day are ineffective. The application of other oxidizing chemicals (e.g., bromine, ozone, hydrogen peroxide, and potassium permagenate) is restricted because they are costly, environmentally prohibitive, or impractical to distribute throughout a cooling system.

#### CLAM-TROL CT-1: NONOXIDIZING MOLLUSCICIDE

Clam-Trol CT-1, patented for use as a nonoxidizing molluscicide, is a water miscible formulation containing two cationic surfactants: alkyldimethylbenzylammonium chioride (Quat) and dodecylguanidine hydrochloride (DGH). Clam-Trol CT-1 is USEPA registered for use as a molluscicide for once-through and recirculating cooling systems. This molluscicide presents two significant features: the ability to eradicate mollusks, like Zebra mussels, when applied for only 6 to 24 hr and the ability to be neutralized prior to discharge.

#### CT-1 Applications: Zebra Mussel Fouling Control

This molluscicide presents an unique advancement in the art of macrotouling control; Clam-Trol CT-1 eradicates adult and juvenile Zebra mussels in cooling systems using feasible, cost effective, treatment regimens. When applied, CT-1 remains substantially undetected by the mussel, which siphons in a lethal dose during an application period of 6 to 24 hr (depending on dosage and water temperature). A delayed mortality response occurs following the brief exposure period.

Periodic applications during the spawning and mussel setting period from May to September will provide effective control of Zebra mussel fouling. Treatment applications will focus upon the eradication of juvenile mussels to prevent their growth to adult size and to prevent the accumulation of mussel encrustations within the cooling system. Once the juvenile mussels expire, they will detach and pass through the cooling system. The fire quency of applications (2 to 4 times/year) will be #.te specific for each cooling system since the degree of mussel infestation will vary from one system to another. A monitoring program to determine the extent and degree of mussel infestations can be established by using monitoring devices (i.e., Betz Macrotracker) and suspending substrates located near cooling system Intakes. The degree of infestation, rate of mussel growth, and the the effectiveness of molluscicide applications can be monitored with these surveillance devices.

#### **Environmental Considerations**

In contrast to continuous chlorination, Clam-Trol CT-1 treatment regimens have short application periods, small product volume requirements, and can be readily neutralized by either passive or active processes. Both CT-1 actives (Quat and DGH) are short-lived because they are readily adsorbed by naturally occurring substrates including slits, clays, suspended solids, humic acids, and even the microfouled surfaces of cooling systems. Studies (10) have shown that once the actives are adsorbed, they no longer exhibit toxicity. If required, CT-1 applications can be actively detoxified by applying a blend of clays (Betz DT-1) to the treated water (11).

Clam-Trol CT-1 treatment programs are designed to maximize the passive neutralization of the actives within the cooling system. For example, a segmented treatment approach is often used to focus applications to specific areas or system components. Molluscicide requirements are further minimized by reducing flow rates or using static treatments where possible.

To obtain discharge permitting approval from a state regulatory authority, an application package would include: a description of the macrofouling problem to the power plant and the need for control, CT-1 product description (constituents, MSDS, and aquatic toxicity data), CT-1 application procedures and expected discharge concentrations, a description of the monitoring program during treatments, and a description of the detoxification program (if needed).

#### Application Experience: Asiatic Clam Macrofouling

Since 1986, Clam-Trol CT-1 treatment programs have been providing state-of-the-art macrofouling control for fouling caused by Aslatic clams in freshwater cooling systems (12). Seasonal applications (2 to 4 times/year) provide a preventative treatment program by focusing upon the eradication of juvenile clams and preventing their growth to adult fouling size. The eradication of juvenile clams that colonize intake bays has eliminated the need for annual cleanouts of adult populations and prevents the threat of forced outages due to macrofouling at power plants (13). Seasonal CT-1 applications of 12 to 24 hr to the safety related and service water systems of nuclear power plants are also providing a better control alternative than continuous chlorination to assure the unobstructed operation of these systems (14). In addition, industrial facilities are employing Clam-Trol CT-1 treatment programs for the eradication and control of Asiatic clams for their entire process systems. The application experiences for Asiatic clam macrofouling control treatment programs are directly applicable to the developing Zebra mussel fouling control programs.

#### LABORATORY EFFICACY STUDIES: ZEBRA MUSSELS

#### Methods

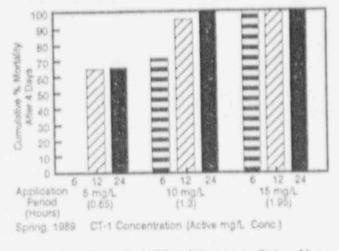
Zebra mussels, 10 to 20 mm in size, were collected from the intake canal of a power plant in Lake Erie in 1989 when amblent water temperatures were 5 to 7 °C. The mussels were shipped in these cold water conditions to Betz' Aquatic Toxicology Laboratory in Trevose, Pennsylvania. The mussels were fed twice a day with algae and gradually accorded over several weeks in recirculating culture chart bers to three temperature regimes: 11 °C, 15 °C, and 20 °C.

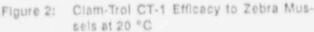
For the efficacy evaluations 20 to 25 mussels were transferred to 5-L glass aquarla and given a 24-hr acclimation. period. Mussels that did not reattach within the test aquaria and were not actively siphoning were removed. Static renewal bloassays were initiated by replacing the culture water with different concentrations of Clam-Trol CT-1 test solutions: 0 mg/L (Control), 5 mg/L, 10 mg/L. and 15 mg/L. Following exposure periods from 6 to 24 hr for each test concentration, randomly selected test aquaria were renewed with fresh culture water. Delayed montality responses were monitored for several days following each exposure. Mortality determinations were recorded when the bivalve shells were gaped open and did not respond to gentle prodding. In many cases evidence of tissue putrefaction was noticed. Mussels that were alive in the control and treatment tests were usually actively siphoning.

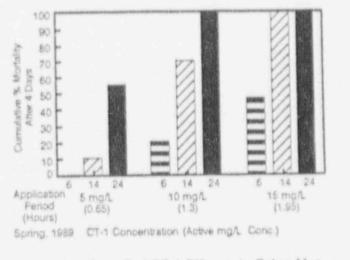
#### Results

The mortality responses of these laboratory efficacy evaluations correlated with CT-1 dosage, exposure period, and water temperature. Figures 2, 3, and 4 present the cumulative mortality responses 4 days after the CT-1 applications. Note that Clam-Trol CT-1 contains 13% total active concentration. Thus, Clam-Trol CT-1 concentrations of 15 mg/L, 10 mg/L, and 5 mg/L contain total active concentrations of 1.95 mg/L, 1.3 mg/L, and 0.65 mg/L, respectively.

At 20 °C (see Figure 2) mortality responses of 70% and 90% were achieved at 10 mg/L as CT-1 for exposures of 6 hr and 12 hr, respectively. A 6-hr application of 15 mg/L as CT-1 caused a 100% kill at 20 °C. At 15 °C a 6-hr application at 15 mg/L CT-1 caused 50% mortality and a 14-hr, application at 15 mg/L CT-1 achieved 100% mortality (see Figure 3). The 10 mg/L CT-1 applications for 6-hr, 14-hr, and 24-hr caused 20%, 70%, and 100% mortality responses respectively, at 15 °C. Then, at 11 °C efficacy data becomes more variable, but 12- and 24-hr applications of CT-1 at 15 mg/L achieved 80% to 95% mortalities (see Figure 4).







#### Figure 3: Clam-Trol CT-1 Efficacy to Zebra Mussels at 15 °C

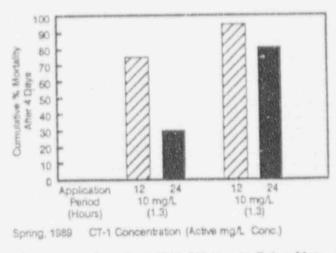


Figure 4: Clam-Trol CT-1 Efficacy to Zebra Mussels at 11 °C

#### FIRST ZEBRA MUSSEL TREATMENTS

Two innovative treatment programs employing CT-1 applications for Zebra mussel fouling control were conducted at Detroit Edison Company's Enrico Fermi II Nuclear Power Plant and Consumers Power Company's J. R. Whiting Power Plant. Both power plants are located hear Detroit, use Lake Erie water in thei/cooling systems, and were experiencing Zebra mussel infestations necessitating preventative fouling control measures. These first Clam-Trol CT-1 applications were conducted In November/December of 1989 during a period when ambient lake water temperatures declined to below 5 \*C. These severe temperature conditions were expected to hamper optimal treatment programs. Biomonitoring of treatment effectiveness was conducted at both power plants. The effectiveness was correlated with CT-1 desage and water temperature.

# CONSUMERS POWER COMPANY J. R. WHITING STATION

#### Background

The J. R. Whiting station, a 3-unit (350 MW), coal-fired generating power plant, first reported Zebra mussels within plant water systems in July 1989. The mussels were initially noticed uniformly attached to the concrete walls of the plant's oil-water (API) separator at a density of 1 mussel per 4 In<sup>2</sup>. A rapid intestation occurred during the following 4 – 6 weeks. The fish deterrent nets situated across the intake canal became so infested with attached mussels that the weight of the mussels caused the nets to be pulled from the bottom due to the restricted flow through the nets. During one week, the nets had to be changed twice.

In September an accumulation of mussels in Unit 1 contributed to a shutdown for cleanout and repair of equipment. Approximately 4 ft<sup>3</sup> to 6 ft<sup>3</sup> of Zebra mussels were also found in the house service water system. The water flow to the boller feed pumps had been restricted by mussel clogging. These blockages required that feed pumps be switched and cleanouts be scheduled during the weekends when load was reduced. Figure 5 shows extensive fouling and impingement of mussels at the inlet side of a cooling loop. It also shows many of the tubes plugged with mussels on the outlet side.

This mussel Infestation created extensive macrofouling conditions that threatened equipment operation and jeopardized plant availability. A molluscicide treatment control program was designed to eradicate the Zebra

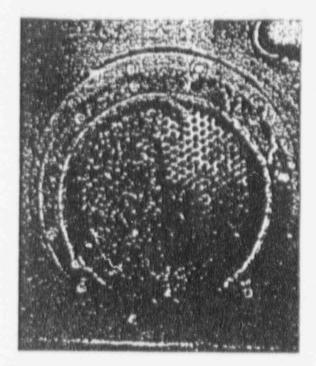


Figure 5: Zebra Mussel Fouling of a Cooling Loop, J. R. Whiting Station

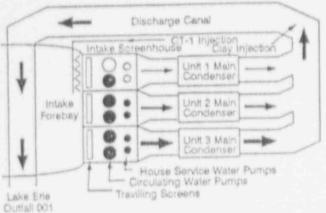
mussels and meet environmental discharge requirements. This program was implemented in December of 1989.

#### Molluscicide Application Procedures

Treatment of the Whiting station consisted of several procedures including segmented treatment approach, flow rate reduction of treated systems, detoxitication, and recirculation of heated cooling water to the intake to raise the ambient water temperature. These procedures helped minimize the amount of molluscicide required and meet the discharge permit requirements. They also increased the efficacy of CT-1 applications.

As part of the segmented treatment approach, separate molluscicide applications were fed to each of the three main condenser circulating water systems and the service water system. Each system received a 12-hr CT-1 application. Figure 6, a schematic of the Whiting cooling systems, shows three separate intake bays — each corrisisting of two main circulatory pumps and two service water pumps. Since all six service water pumps feed to a common header, only a single feed point was required to apply Clam-Trol CT-1 to the service water system.

For each of the main circulating systems, CT-1 was applied directly with a sparge header, which was positioned in front of the Intake bays, upstream of the travelling screens. To minimize the amount of CT-1 fed, only one of two main circulating pumps was operated; this reduced the flow rates to the unit being treated. Table 1



Dunial dos

Figure 6: J. R. Whiting Plant, Consumers Power Company

Table 1: J. R. Whiting Station, December 1989

	System	Reduced		Cor-Trol CT-1 Analysis				
	Flow Rates (GPM)	Flow Rate Treated* (GPM)	Application period (hr)	(mg/L)	Max. (mg/L)	Avg. (mg/L)	Outtall (mg/L)	
Unit 1	68,000	33,000	12	4.3	13.9	8.9	ND <sup>b</sup>	
Unit 2	65.000	33,000	12	12.6	17.0	14.8	ND	
Unit 3	90,000	45,000	12	11.5	16.5	14.3	ND	
SWS4	3,400	3,400	12	ND	38.0	14.3	ND	

 Flow rate was reduced by operating only one of two circulating pumps. This minimized the cooling water being treated.

- ND \* Nondectable (< 0.1 mg/L as Ciam-Trol CT-1 or < 0.02 mg/L total active concentration).
- SWS = Service Water Syntem
- The feed pump to the service water system was inoperable for short duration.

presents the flow rates of each unit, the reduced flow rates of the treated cooling water during the 12-hr application period, and CT-1 concentrations measured within the system being treated and at the outfall to receiving waters.

All the cooling water from each system converges at the inlet end of the 1/4 mile discharge canal. The mixing of the treated water with the untreated cooling water helped reduce the residual CT-1. Detoxification of the remaining CT-1 residual was achieved by feeding Betz DT-1 (a blend of bentonite clays) directly to the discharge canal. The clays were feed rate of 1 mg/L of clays for each 1 mg/L of residual CT-1 to be detoxified. The average clay concentrations fed during the treatments of Units 1, 2, and 3 were 5.9 mg/L, 6.7 mg/L, and 8.8 mg/L respectively.

Detoxification of the service water system application was not required because treated water was rerouted and diluted within the plants' ash ponds. Residual CT-1 was measured using an analytical photometric method (15) with a detection limit of 0.1 mg/L as ClamTrol CT-1 (or 0.013 mg/L as total active concentration). All outfall samples collected during each 12-hr application were nondetectative (< 0.1 mg/L).

To increase the amblent intake water temperature, a portion of the heated discharge water was recirculated to the intake canal during molluscicide application periods, increasing the siphoning and metabolic activity of the Zebra mussels by sievating the intake water temperature would aid in increasing the mortality responses. The ambient intake water temperatures were between 0 °C and 2 °C. The recirculated water provided a  $\Delta$  T between 2 °C to 6 °C.

#### Results of J. R. Whiting Applications

Each of the molluscicide applications at the J. R. Whiting station was assessed with biomonitoring procedures. Flow-through bioboxes were positioned at the inlet and outlet ends of the treated cooling systems (see Figure 7). Approximately 40 – 80 Zebra mussels measuring 4 – 20 mm were placed in each biobox. Constant water flow was maintained through the bioboxes during each of the 12-hr applications and for several weeks following each application to monitor delayed mortality responses. Mussels were dead when the bivalve shells gaped open and did not close when gently prodded. The control mussels had cumulative mortality responses of 0 to 2% for the duration of the monitoring period.

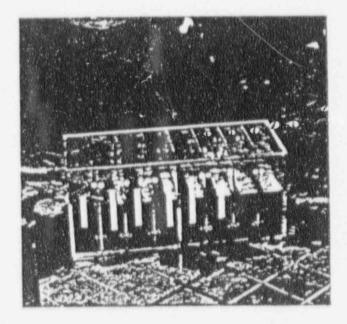


Figure 7: Flow Through Bloboxes for Monitoring the Efficacy of Applications

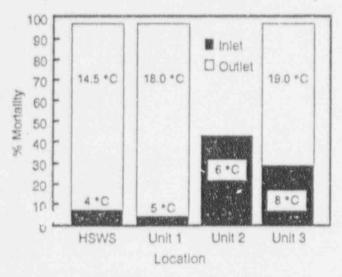
The mortality responses, which were monitored at the inlets and outlets of the units treated with 12-hr CT-1 applications, correlated with water temperatures (see Figure 8). Mortalities of greater than 95% were achieved at the outlets of units where water temperatures ranged from 14.5 °C to 19 °C. At the inlets of the service water system and at Unit 1, mortality responses of 5% or less resulted when the water temperatures never exceeded 4 °C or 5 °C. Units 2 and 3 had inlet water temperatures of 6 °C and 8 °C; their mortality responses were 43 and 26%.

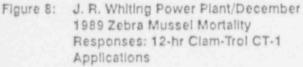
#### DETROIT EDISON COMPANY ENRICO FERMI II NUCLEAR POWER PLANT

#### Background

The Enrico Fermi II Nuclear Power Plant is a single-unit (1100 MW) facility with a recirculating cooling system (see Figure 9). The main circulating cooling water flows from the cooling pond through the main condensers to the hypert is cooling towers, then returns to the cooling pond. The makeup water to the cooling pond originates in the once-through service water system, which uses raw water from Lake Erie. The decant or blowdown pipe of the cooling pond is the point of discharge to Lake Erie.

Zebra mussels were first found colonizing the concrete walls of the service water intake structure in late August, 1989. Diver Inspection of the intake structure revealed uniform populations of 20,000 mussels/m<sup>2</sup>. Subsequent inspections of the service water components during the refueling outage (September – November, 1989) revealed mussels attached to the service water pump casings, reaction building closed cooling water heat





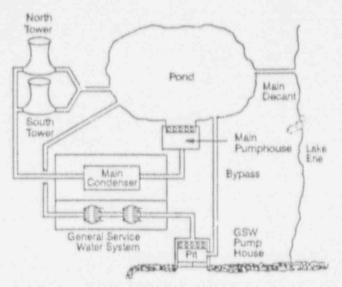


Figure 9: Enrico Fermi II Nuclear Power Plant, Detroit Edison

exchangers, and main turbine lube oil coolers. All Zebra mussels were juveniles from 3 to 5 mm in size.

#### Molluscicide Application Procedure

Clam-Trol CT-1 was applied at the service water pump Intake for 15 hr. This application was initiated when the intake water temperature was 4 °C. The Intermittent chlorination treatment for the service water system was terminated 24 hr prior to feeding Clam-Trol CT-1. This procedure was necessary because Zebra mussels will close their bivalve shells in the presence of chlorine and thus would not be actively siphoning during the CT-1 application.

To prevent any release of residual CT-1 to Lake Erie, the cooling pond blowdown was terminated and the service water pump suction was switched from Lake Erie to the cooling pond. CT-1 was applied directly into the service water pump suction plt via a sparge header. The entire service water flow enters the cooling pond and provides a significant dilution of the CT-1 treated water. To provide further neutralization, the service water pump suction remained in recirculation mode (suction from cooling pond) for 10 hr after CT-1 application. To complete the neutralization process, dry clays (Betz DT-1) were fed to the cooling pond.

The fire protection system was statically treated during this service water application. The fire protection pumps take a suction from the service water pump pit. Treated CT-1 service water was fed to the fire protection system upon analytical verification of a targeted 20 mg/L CT-1 concentration in the service water. The fire protection system was closed once the CT-1 application was injected into the system.

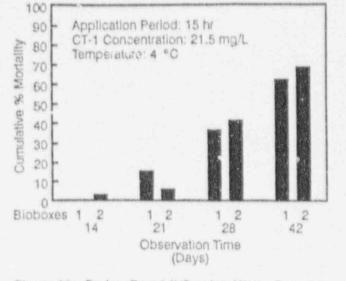
#### **Results of Fermi II Applications**

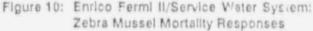
Two flow-through bloboxes were positioned within the service water system to monitor the efficacy of the 15-hr application. Each blobox contained approximately 60 – 100 mussels and received service water continuously during the application and for 42 days following the application to monitor the delayed mortality response. Clam-Trol CT-1 was analytically determined each hour during the application (See Table 2). The average CT-1 concentration was 21.5 mg/L.

Figure 10 presents the delayed mortality responses following the molluscicide application. The 4 °C water temperature causes a slow mortality response. On day 27 the delayed mortality responses were 39 and 42%. The final mortalities of 62 and 73% were achieved on day 42. The higher mortality responses for the Fermi II application compared to the inter responses at the Whiting Station can be correlated with a higher CT-1 dosage (21.5 mg/L at Fermi II instead of approximately 15 mg/L dosages at the Whiting Station) and a longer application period (15-hr at Fermi II instead of 12-hr at the Whiting Station).

Table 2:	Fer.nl II Nuclear Power Plant CT-1 Analy-
	sls of The Service Water System

Sampling Time During Treatment (in hr)	CT-1 (in mg/L)
0.0	
0.5	14.1
1.0	15.2
2.0	17.7
3.0	18.3
4.0	27.7
5.0	21.0
6.0	27.8
7.0	26.3
8.0	18.6
9.0	21.8
10.0	21.0
11.0	21.6
12.0	22.0
13.0	23.2
14.0	24.3
15.0	23.7
Treatment Stopped	Average = 21.5 mg/L





#### CONCLUSIONS

The objectives of a Clam-Trol CT-1 treatment program for Zebra mussel fouling control is to eradicate the juvenile mussels and to prevent the accumulation of mussels within the cooling system. The frequency of applications (2 to 4 times/year) required to achieve proper macrotouling control will be site specific for each cooling system. Certain systems and specific components may require more frequent applications. A mussel surveillance program to monitor the occurrence and extent of mussel infestation and their growth within a cooling system is recommended as an integral part of the overall procedure for a Zebra mussel fouling control program.

If Zebra mussels are known to be colonizing a particular area within the general geographic region of a power plant, the following steps are recommended:

- Step 1: Establish a mussel surveillance program at the cooling water intakes and within the cooling system, particularly, at the safety-related and service water systems.
- Step 2: Develop a treatment strategy for applying the molluscicide to provide fouling control and also to meet discharge permit requirements. Implement procedures to obtain approval with the regulatory authorities. Note that approval can often take several weeks.
- Step 3: Maintain a vigilance of the fouling. Zebra mussel fouling can abruptly develop into advanced fouling that may require a cleanout of the system before protective treatment program initiation.

i

Step 4: Apply Clam-Trol CT-1 treatments based upon the extent of mussel infestation. Optimize the CT-1 applications (6 to 12 hr) when water temperatures are ≥ 15 °C.

At Fermi II a preventative treatment program was implemented to eliminate any impediment to water flow of the once-through service water system. Preventing macrofouling within this service water system is essential for the operation of this nuclear facility. The initial 1989 CT-1 application provided mortality responses of 62% to 73% when the water temperatures were 4 °C. Applications will be resumed in the spring of 1990 based upon a mussel surveillance program.

At the J. R. Whiting station Zebra mussels are well established within the vicinity of this power plant and will require a regimented molluscicide treatment program to protect equipment and maintain plant availability. CTwas fed in segmented applications (12 hr or less) and the amount of molluscicide was minimized by reducing flow rates. This provided an effective means of controlling the chronic infestation at this facility. In addition, the detoxification potential of this molluscicide provided a means of eliminating toxicity at the discharge.

The monthly Lake Erie water temperatures measured at the Intake of the J. R. Whiting Station from May through September were 15 °C or greater (see Figure 11). It is during this period that spawning activity and infiltration of Juvenile mussels or veligers into cooling systems occurs. Therefore, most treatments should be applied between May and September for optimal fouling control. Optimizing preventative treatment programs by applying Clam-Trol CT-1 for 12 hr or less can be successfully accomplished when water temperatures are 15 °C or greater. This has been demonstrated by mortality

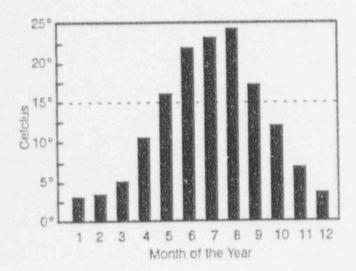


Figure 11. Lake Erle Inlet Temperature: J. R. Whiting Power Plant

responses of >95% achieved at the condenser outlets of the J. R. Whiting station (see Figure 8) when watartemperatures ranged from 14.5 °C to 19 °C and from the laboratory efficacy studies conducted at 15 °C and 20 °C (see Figures 2 and 3). Even CT-1 applications as brief as 6 hr when water temperatures are 20 °C should provide effective treatments in July and August.

When Clam-Trol CT-1 must be applied during the colder months of the year, longer treatment periods of 24 to 72 hr will be required or intake temperature should be elevated to  $\geq$  15 °C by recirculating the heated cooling water.

The threat posed by the Zebra mussel has been welldocumented. In this paper we have described a very practical and cost effective treatment program that has been successfully applied at two power plants. The effect of water temperature on the treatment is important and is also thoroughly reviewed here. Successful Zebra mussel control in power plants is achievable.

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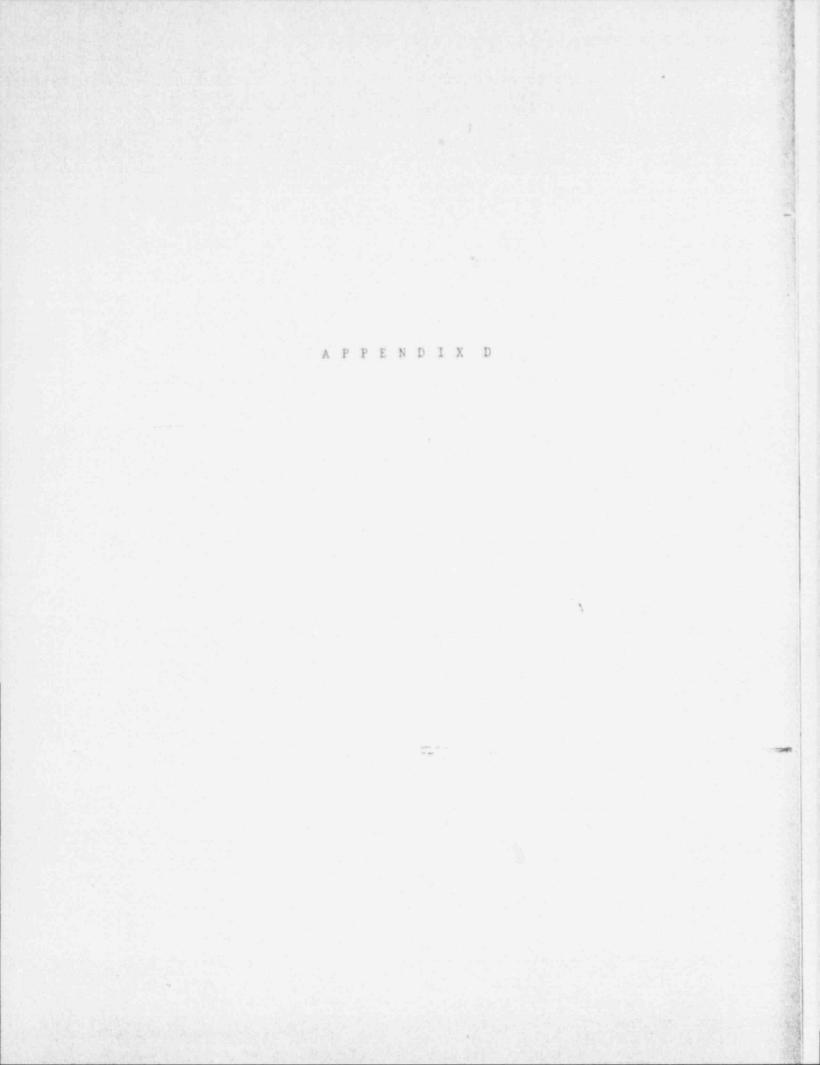
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- \*Determination of Clam-Trol CT-1 b<sub>x</sub> is used.
   Photometric Methyl Orange Complexation Procedure\*, Betz Laboratories Anai c<sup>-</sup> Method\* B is Laboratories, Inc., Trevose, PA, 1, 3<sup>o</sup>







LABORATORIES, INC.



SOMERTON ROAD TREVOSE, PA 18047 U.S.A / TEL 215-355-3300 TELEX: 173 148 FAX # 355-2669

Aquatic Toxicity Report

Clam-Trol CT-1

Rainbow Trout : 96 hr LC50 = 14.7 mg/1

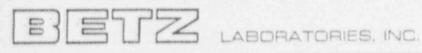
Bluegill Sunfish : 96 hr  $LC_{50} = 4.3 \text{ mg/l}$ 

Fathead Minnow : 96 hr LC50 = 2.9 mg/1

Daphnia magna : 48 hr  $LC_{50} = 0.4 \text{ mg/l}$ 

Note: The above LC<sub>50</sub> values represent toxicity levels for Clam-Trol CT-1 when 100% of the "free" actives are available to the aquatic organism (that is, no suspended solids for adsorption of the actives).

When Clam-Trol CT-1 is exposed to adsorbent material (i.e. clays, silts, suspended solids, humic acids, etc.), acute toxicity as well as chronic toxicity is eliminated or greatly reduced due to the adsorption properties of the active ingredients.



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BETZ LABORATORIES, INC. 4636 SOMERTON ROAD, TREVOSE, PA. 19047

PRODUCT: CLAM-TROL CT-1

8/22/90

AQUATIC TOXICOLOGY

SHEEPSHEAD MINNOW

96 HR. LC50: 7.0 MG/L

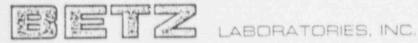
MYSID SHRIMP

96 HR. LC50: 1.45 MG/L

1811 - 1 11 100 -

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03

SOMERTON ROAD TREVOSE, PA 19047-US A / TEL 215-355-3300 TELEX, 173 148-FAX # 355-2868

Society of Environmental Toxicology and Chemistry (SETAC) Presented November 9-12, 1987 at Pensacola, Florida Meeting

DETOXIFICATION POTENTIAL OF A NEW MOLLUSCICIDE FOR ASIATIC CLAM FOULING CONTROL.

L. A. Lyons, Betz Laboratories, Inc. Trevose, PA.

A new molluscicide to control Asiatic clam biofculing in cooling and service water systems has several environmentally desirable features. Seasonal applications, requiring short treatment periods of only 24 hours, provide effective clam fouling control as opposed to continuous chlorination treatments. Another feature is the detoxification or neutralization potential of the molluscicide by adsorption. The actives in the molluscicide are short-lived because they are readily adsorbed by a variety of materials and substrates. Once these actives are adsorbed, they no longer exhibit acute toxicity. Thus, passive adsorption of the actives within the system can detoxify the treated water, or the treated water may be detoxified prior to the point of discharge.

The LC50's of the new molluscicide to Daphnia magna, fathead minnows and rainbow trout are 0.4 mg/1, 3.0 mg/1, and 14.7 mg/1, respectively. Molluscicide concentrations ranging from 10.0 mg/1 to 50.0 mg/l were treated with several kinds of potential sorptive detoxification media. A series of bioassays with Daphnia magna and fathead minnows were conducted immediately following these detoxification treatments. Determinations of the rate of survival from these detoxification treatments are provided.

# Methods:

Clam-Trol CT-1 solutions were mixed for 5 minutes with potential detoxification media in glass aquaria. Aliquots (200 mL) of the mixture were removed from the aquaria for daphnid testing. Fathead minnows were placed in the aquaria. The detoxification potential was determined from the resultant mortality response.

			Fathead Minnow - Cumulative % Mortality			Daphnia magna - Cumulative % Montality		
Clam-Troi CT-1 (mg/l)	Active Clay (mg/l)	Clay: Clam-Troi	4 hr	24 hr	48 hr	6 hr	24 tv	48 hr
Control			0	0	0	0	0	0
10	-	-	100	100	100	100	1.00	100
-	100	-	0	0	0	0	0	0
10	10	11	0	0	0	35	100	100
10	20	2.1	0	0	C	0	85	1 100
10	30	31	0	0	0	0	30	30
10	50	5 1	0	0	0	0	0	0
10	100	101	0	0	0	0	0	0

# Detoxification of Clam-Trol CT-1 with Bentonite Clay

8

## Detoxification of Clam-Trol CT-1 with Humic Acid

			Fathward	Minnow - Cum Mortality	ulative %	Daphni	a magna - Cun	mula ( I've
Glam-Trol CT-1 (mg/l)	Humic Acia (mg/l)	Humic: Clam-Trol	24 hr	48 hr	96 hr	1 hr	24 hr	48 hr
Correro	-	-	0	0	0	0	0	0
10	-		. 0	100	100	0	100	100
-	250		0	0	0	0	0	0
10	30	3 :	0	¢	0		-	
10	50	5.1	0	0	0		inter a second sec	
10	100	10.1	Q	0	0	0	30	100
10	200	20:1	0	0	0	0	0	15
10	2.50	25.1	. 0	0	0	0	0	0

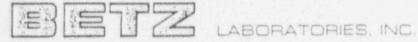
## Detoxification of Clam-Trol CT-1 with Activated Carbon

			Fatheed Mixmow - Cumulative % Mortauty			Daonnia magna - Cumulatina % Mortality		
Clam-Trol CT-1 (mg/L)	Actived Carbon (mg/L)	Carbon: Clam-Trol	4 hr	24 hr	96 hr	4 hr	24 hr	48 hz
Control	-	-	0	0	0	0	0	0
-	12.5	-	0	0	0	0	5	5
	25	10.0	0	_0. `	٥	0	0	10
10	-	-	100	100	100	100	100	100
10	12.5	1.25.1	Ó	0	0	0	100	100
10	25	2.5 1	0	0	0	Ö	0	20
25	12.5	1.2	0	0	0	90	100	100
25	25	1.1	0	Ö	0	100	100	100

#### Detoxification of Clam-Trol CT-1 with Magnesium Silicate (Synthetic)

			Fallward Minnow - Cumulative % Mortality			Deprinte megne - Cumula tres % Mortailty		
Clam-Troi CT-1 (mg/L)	Mg Silicate (mg/L)	Mig Silicatus: Clasm-Troi	24 hr	44 hr	72 hr	1 hr	24 hr	48 hr
Control		-	0	0	0	0	0	0
10		-	100	100	100	0	100	100
-	100		Q	0	0	0	0	0
10	5	1.2	20	40	40	0	100	100
t0	10	1.1	Q	0	0	Q	100	100
10	20	2.1	0	20	20	0	100	100
10	30	1	0	0	0	0		1 4.6.

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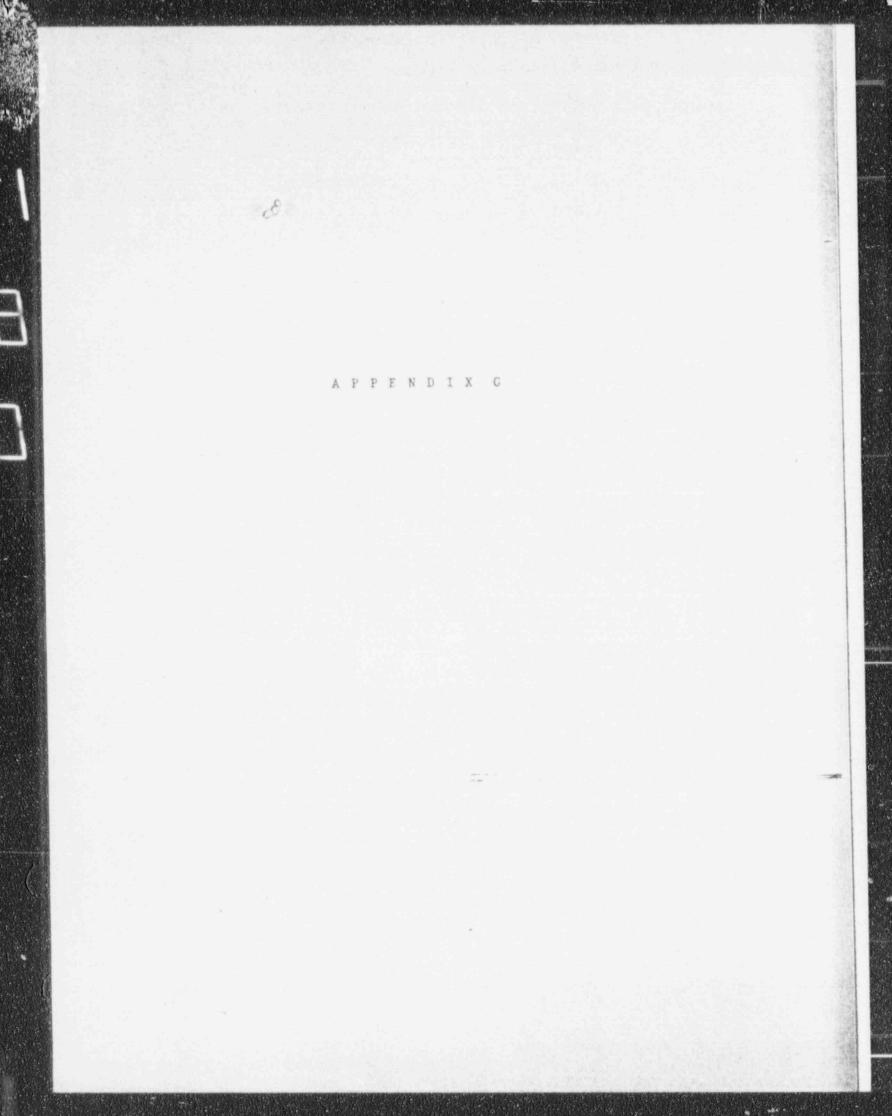
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#### CHRONIC EFFECT OF DETOXIFIED CT-1 ON FISH SURVIVAL AND GROWTH

The chronic effect of Clam-Trol CT-1 detoxified with Betz DT-1 was studied using the standard 7-day chronic fathead minnow survivability and growth rate test. The data presented in Table 6 show that 10 mg/L of CT-1 resulted in 100% mortality of the minnows. The addition of Betz DT-1 at a 1:1 ratio with CT-1 completely eliminated chronic mortality effects on fathead minnows, but allowed some growth rate impairment. Ratios of DT-1 to CT-1 of 3:1 or greater completely eliminated any effect of CT-1 on both minnow survivability and growth.

			Me	ean Fath	nead
ng CT-1/L	mg DT-1/L	Mortality (%)	Dry	Weight	(mg±SE)
0	0	5		0.3101	(0.0157)
0	100	0		0.2855	(0.0015)
10	0	100*		THE THE CO. WAS ARE AND	ar waa dan am am am am am am 🕸
10	10	13		0.1881	(0.0242)*
10	30	_ 7		0.3032	(0.0158)
10	50	18		0.3355	(0.0046)
10	100	10		0.2811	(0.0112)

Mortality and growth of the fathead minnow (Pimephales promelas) after a 7-day exposure to ratios of Betz Clam-Trol CT-1 and Betz DT-1.



BETZ LABORATORIES, INC.



EDMERTON ROAD TREVOSE, PA 18047-US A / TEL 215-355-3300-TEL2K, 1731-48-FAX #355-2865

#### EFFECT OF CT-1 ON BENTHIC ORGANISME

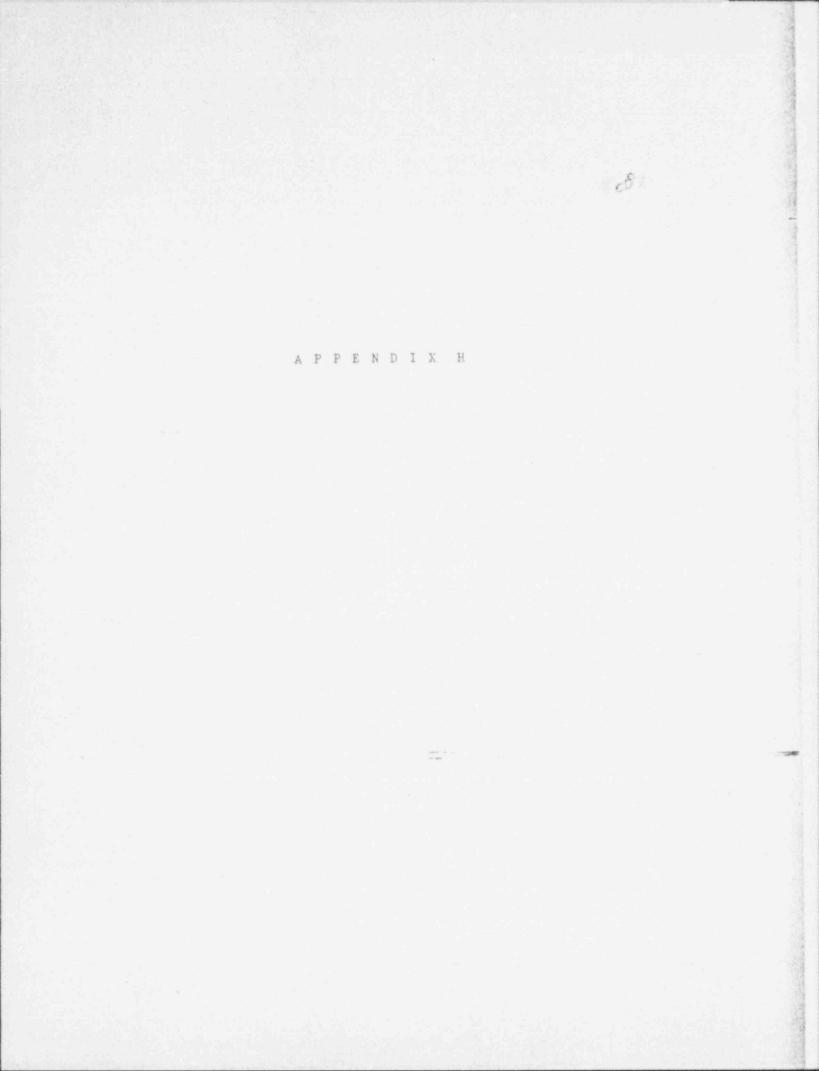
The term "benthic" refers to organisms that live in the bottom sediments of lakes and streams. Aquatic insects such as the midge larva (<u>Chironomus riparius</u>, a 2-winged fly or gnat), are commonly used to study the effects of materials on bottom-living organisms.

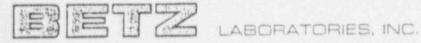
Midge larvae were exposed for 48 hours to 10 mg/L of Clam-Trol CT-1 and to Clam-Trol CT-1 which was detoxified by the addition of Betz DT-1, a blend of highly adsorbent clays. The results, shown in Table 5, indicate that the Clam-Trol CT-1 by itself produced an 80% mortality without detoxification. Treatment with Betz DT-1 in ratios of 1:1 to 1:10, successfully eliminated any effects of CT-1 on the mortality and growth rate of the midge larvae.

Mortality and growth of midge larva, <u>Chironomus</u> <u>riparius</u>, aftar a 2-day exposure to ratios of Betz Clam-Trol CT-1 and Betz DT-1 followed by recovery for 8 days in dechlorinated laboratory water at 20°C. (n=30)

mg CT-1/L	mg DT-1/L	Mortality (%)	Mean Chironomid Dry Weight (mg±SE)	
0	0	0	0.9048 (0.0121)	-
0	100	0	0.9789 (0.0136)	
10	0	80*	0.8121 (0.0135)*	
10	10	10	0.8748 (0.0122)	
10	30	0	0.9164 (0.0112)	
10	50	Э	0.9278 (0.0115)	
10	100	0	0.9502 (0.0180)	

\*Significantly different from controls (a=0.05, Dunnett's test)







SOMERTON ROAD+TREVOSE, PA 19047-U.S.A. / TEL 215-355-3300-TELEX, 173 148-FAX # 355-2869

Aquatic Toxicity Report

#### Determination of the Effect of Detoxified Clam-Trol CT-1 - A Long Term Study Using Fathead Minnows and Daphnia magna

Study Conducted By:

Aquatic Toxicology Laboratory Betz Laboratories, Inc. Trevose, PA

objective:

The purpose of t's study was to determine if any acute toxicity would be exhibited from long term exposures of Clam-Trol CT-1 detoxified with bentonite clay to fathead minnows and <u>Daphnia magna</u> and to determine any evidence of desorption of the actives to a toxic form under these test conditions.

The detoxification of the biocidal activity of Clam-Trol CT-1 is readily achieved by adsorption with a variety of materials and substrates. Once the two cationic actives present in Clam-Trol CT-1 are adsorbed, they no longer exhibit toxicity. The intent of this study was to detoxify toxic levels of Clam-Trol CT-1 and expose aquatic organisms for an extended period to evaluate any acute toxic effects of the detoxified solutions and if any potential description of the actives resulted to cause toxicity.

Test	Organisms:	Fathe	ad m	innov	( <u>Pim</u>	epha	les	DIC	omelas	
		- Sou	rce:	SP	Engin	eeri	ng,	No.		
		- Tot	al 1	engt:	1 (mea	n):	3.5	- 25	0.34	Cin
		- WET	wei	ght	(mean)	1	0.42	-	0.19	Ç.

Daphnia magna - Source: Stock culture - Age: 12 ± 12 hr. old megnates

Test Type/ Conditions: Fathead minnow and  $\underline{D}$ , <u>magna</u> were exposed to the following five treatments and test conditions for 20 days.

Static Renewal Treatments

- control 0 mg/l Clam-Trol CT-1
- 25 mg/l Clam-Trol CT-1
- 25 mg/l Clam-Trol/250 mg/l bentonite clay
- 250 mg/l bentonite clay only

Static Treatment

- Continuously aerated 25 mg/l Clam-Trol CT-1/ 250 mg/l bentonite clay.

#### Method: <u>30-day Fish Test</u>

Detoxified Clam-Trol CT-1 solutions were prepared by mixing 25 mg/l Clam-Trol CT-1 solution with 250 mg/l of bentonite clay (a CT-1 to clay ratio of 1:10).

The two materials were mixed with a mechanical stirrer at 1100 rpm for 30 minutes. All treatments with clay were mixed in the same manner. Fifteen liters of solution were prepared for each treatment replicate.

Twenty fish were exposed to each treatment--two replicate and 10 fish per 15 liter of solution.

All treatments with exception of the continuously aerated 25 ppm Clam-Trol CT-1:250 ppm bentonite clay were renewed with freshly prepared solutions on the following days through the 30-day test: 1, 4, 8, 11, 15, 22, and 25. The test was initiated or ay one. During the renewal of test solutions, only the upernatant was siphoned from each test container and the sedimentation of clay on the bottom was retained in the container the test. Fresh test solution was added after siphoning and mixed with the existing accumulated clay. Fish were fed commercial flake food daily. Observations of mortality and behavior response were assessed daily.

#### 48-h Daphnia magna Test

Standard 48 hr acute <u>Daphnia magna</u> bioassay tests were initiated only on days that solution renewals were made in the fish test. Daphniids were exposed to subsamples of test solution taken from the fish test containers. During each renewal period, toxicity tests were performed with the freshly made test solutions and with the aged solutions taken from each test container.

Twenty <u>D. magna</u> were exposed to each treatment, 10 individuals per replicate. Mortality was assessed at 1-2, 24, 48 hours.

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Simmary of Results

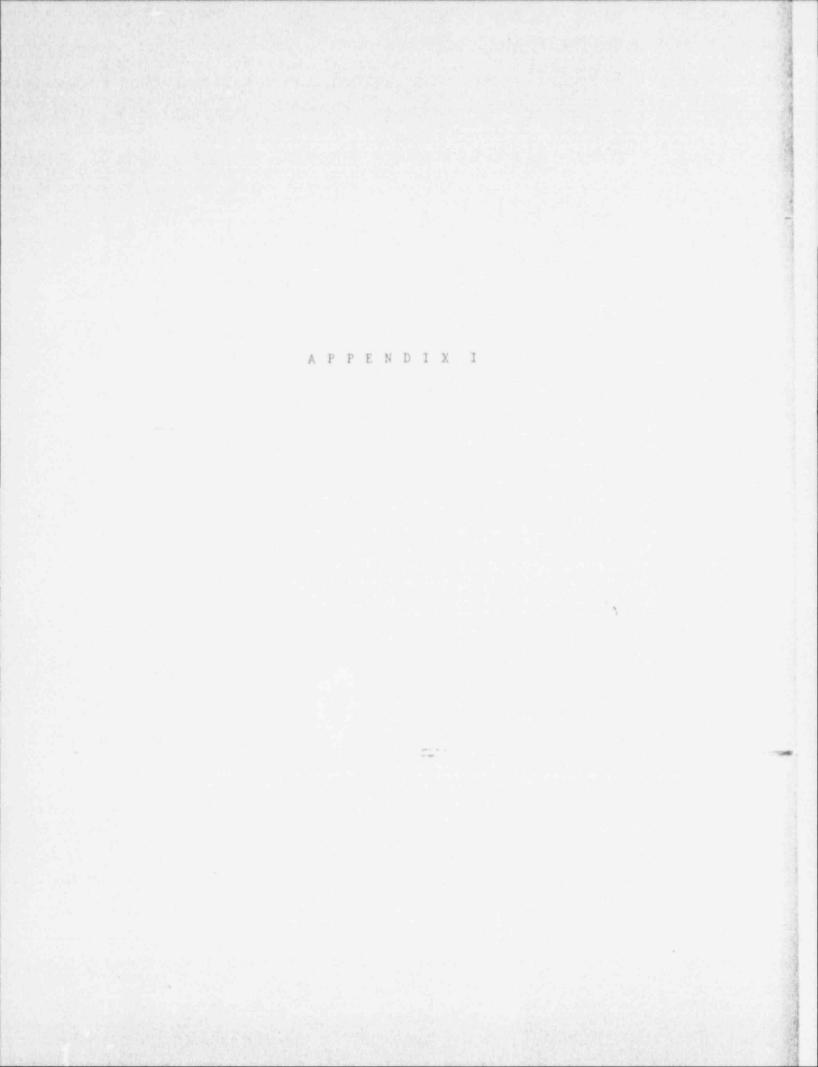
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Detoxified Clam-Trol CT-1 solutions were prepared by mixing 25 mg/l Clam-Trol CT-1 solutions with 250 mg/l of bentonite clay (a CT-1 to clay ratic of 1:10).

No mortality or stress was exhibited to fathead minnows that were continuously exposed for 30 days to detoxified Clam-Trol CT-1 solutions.

No mortality was exhibited to <u>Daphnia magna</u> that were exposed for 48 hour periods to renewed or aged detoxified Clam-Trol CT-1 solutions.

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#### ETTI CLAM-TROL CT-1

## ENVIRONMENTAL INFORMATION PACKAGE

Clam-Trol CT-1 is an effective molluscicide for controlling Asiatic clam macrofouling problems in both once-thru and recirculating cooling systems. The unique molluscicide applications can be used for exterminating adult Asiatic clams which cause advanced stage fouling conditions in cooling systems and can also be used as part of a preventative program for eliminating larvae and juvenile clams before they attain the adult fouling size which can cause advanced fouling conditions. Clam-Trol CT-1 can also be used as a broad spectrum microbiocide for the control of bacterial, fungal and algal slimes.

Clam-Trol CT-1 contains 13% active ingredients of two cationic surfactants and 87% inert materials. The two cationic surfactants are n-alkyl dimethyl bencyl ammonium chloride (Quat) and dodecylguanidine hydrochloride (DGM).



Both straight chain hydrocarbon containing molecules are referred to as surface active agents and have a hydrophobic tail and positively charged molety that readily attaches to membranes to induce biocidal activity. The inert materials of this formulation - ethylene glycol, isopropyl alcohol, and water - are relatively non-toxic to aquatic organisms.

Several studies on the adsorptive characteristics, aquatic toxicity, biodegradation, environmental fate and detoxification processes have been conducted for these cationic surfactants. The results of these studies are summarized herein.

# Adsorption: Ripcida' Mechanism and Adsorption Dates

The toxic properties of cationic surfactants result from a strong interaction with memorane protains. Memorane proteins are essential for many transport mechanisms including various specific ion transport channels. The alkyl portion of these actives becomes imbedded in these memoranes and the charged end disrupts the electrial character of the memoranes. In effect, these cationic surfactants are good biocidal performers but they are short-lived once their positive charge is neutralized upon adsorption to various surfaces.

DGH and Quat have extremely strong affinities for many kinds of suspended material and substrates. A series of laboratory and field studies conducted by the American Cyanamid Company evaluated the degree and rate that DGH is electrostatically bound to suspended matter and other substrates.

In one study, weight portions of sludge containing 5.2% solids obtained from a set a treatment plant were inoculated with 10 ppm and 20 ppm of DGH (1001 stive) and thoroughly mixed. After 1 hour and 24 hours, duplicate samples of the mixtures were centrifuged to separate the solids. DGH was analyzed in the supernatant. The results in the table below show that less than 2 ppm of DGH remained in the supernatant.

DGH added (ppm)	Contact time (hours)	DGE found in supernatant (ppm)
100000000 1111110000000 11111100000000	(Control; water only) 1 24 (Control; water only) 1 24 24 24 24 (Control; water only)	1.2 1.6 1.0 1.0 1.0 1.0 1.7 1.6 1.5

Other laboratory studies utilizing cooling tower water samples from Utah Power and Light demonstrated a loss of 95% DGM in 1/2 hour or less contact time after initial DGH concentrations of 350 ppm, 700 ppm, and 1,750 ppm were added to the samples. The residual DGH (ppm) in the supernatant after precipitates were filtered out and the % loss are provided in the table below:

DGE added (ppm)	Residual DGH (ppm) in Supernatant	t Loss
250 350		95 95
700 700	2 4 3 1	97 96
1750	52 83	01 01 1 - 111

The rate of adsorption (loss of DGH to the cooling tower solids) was also determined from the above sample. Results are presented below:

DGH added (ppm)	Contact time	Residual DGE (ppm) in Supernatant
350	1 6 =- 2 4	28 16 12
1750	1 6 24	82 61 42

Field studies have also demonstrated that DGH is rapidly removed from opoling water systems. The two tables below show the concentration of DGH detected in the cooling tower effluents on two different occassions.

ample	Time		Grease	DGE Content in effluent (ppm)
Addition	8:15 AM		158	. 0 0
(16-17 ppm)	9:20 AM 10:15 AM 12:00 PM		300 700 500	0.4 0.9 0
Makeup Water added			14	
LAKE CLEV, U.	phar a st day has been been been been			Chevron Oil, Salt
	trined volum	e of 350,000	gallons and	a blowdown of 400
dbr . dbr .				
gpn.		Suspended Sclids	Organic Carbon	DGE content in effluent (ppm)
	Time	Suspended	Organic	DGE content
gpn.		Suspended Solids (ppm)	Organic Carbon	DGE content
Sample Before	Time 1:30 PM	Suspended Solids (ppm)	Crganic Carbon (ppm)	DGE content in effluent (ppm)
Sample Before addition	Time 1:30 PM = 13 ppm	Suspended Sclids (ppm)	Organic Carbon (ppm) 17	DGE content in effluent (ppm)

Radioactive labelled Quat solutions at concentrations of .01 to .1 ppm were used for studies conducted by Rohm and Haas Company (Krezeminski, SF, et.al., 1977) to determine adsorptive characteristics to different types of material. In these "C studies, adsorption was measured by types of radioactivity from the labelled solutions exposed to three the loss of radioactivity from the labelled solutions exposed to three different types of adsorbent material - river silt, an aquatic plant, and alum floc. Results are reported below:

	(201 10	tive Quat) Concentrat	ion in Wate	2 (272)
Adsorbent	Contact Time (hr)	Initial	Final	Adsorbed
liver Silt	1/60	0.070	0.006	91
quatic Plant Azolla Carolinia Lum Floc	na) 24 1/2	0.056 0.094	0.008	86 100

As with the DGH studies, field studies conducted by Rohm and Haas have determined the residual Quat concentrations in cooling tower blowdown water at various intervals following biocide application. The adsorptive nature of the active to the surfaces of the cooling system and to particulate material caused a substantial loss.

Hyamine 3500 (50% Active Quat) in Cooling Tower Blowdown Water as a Function of Time After Dosingª Concentration of Hyamine 3500 (ppm) Dose 3 Dose 2 Dose 1 Time After (30 ppm) (30 ppm) (60 ppm) Dosing (hrs) 31.6 25.8 60.0 22.0 21.1 52.2 2.5 14.2 14.8 44.8 2 9.9 10.6 26.5 8 0.041 0.25 5.18 72 0.011 NDR" 2.50 120 NDR 0.008 1.16 168 a) Three consecutive dosings (60, 30, 30 ppm) at one-week intervals b) NDR = no detectable residue; less than 0.005 ppm Cooling tower capacity = 40,000 gallons Blowdown rate = 30 gpm

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#### Bisdecradation

The rate of biodegradation of the Quat active was eval ted in both acclimated and unacclimated microbial cultures (Gawel, 1.J. 2 Huddlestown, R.L., Continental Oil Company, 1972). The microorganisms used for the biodegradation tests were derived from both soil and raw city sewage, and which grew on a defined medium. Rates of biodegradation were determined analytically using an extraction procedure to remove all unde-graded Quat. The results reported below present biodegradation data from cultures acclimated for different time intervals to the Quat (100% active).

Acclimation	None	TO FOLTE	48 Hours	9 Dave
Incubation Period	24 Hr.48 Hr.	24 Hr.48 Hr.	24 Hr.48 Hr.	24 HF.48 Hr.
Percent Decraded	37 95	60 97	60 97	15 50

# EFFECT OF CULTURE ACCULURETON ON QUAR BIODEGRADATION

The reduced rate of biodegradation at 9 days was attributed to the additional transfers of Quat causing an increased biodidal effect upon the cultures.

The Rohm and Haas investigation, previously cited, reported biodegradation studies of Quat conducted by exposing the "C labelled active to activated sludge. Fresh synthetic sewage (nutrients) and labelled Quat were renewed daily except weekends to a closed culture system during a 24 day study period. Biological activity was determined by during the "CO, that was generated from the labelled Quat. In measuring the "CO, that was generated from the labelled Quat. In order to allow for acclimation and any toxic effect, dosing of the labelled active started at 1 ppm and increased gradually over a period of days to 10 ppm. Figure 1 presents the results as the percent "C detected in the supermatant as undegraded active removed from the closed system and the percent "C as "CO<sub>2</sub> converted during biological degradation of the Quat.

During the first two weeks, 80% of all labelled Quat added to the culture unit was converted to "CO2. This activity increased to a 92%

# Acurtic Toxicity: Adsorbed vs. Free Actives

Acute toxicity tests determining LC., values for Clam-Trol CT-1 with 13% active ingredients is provided as follows:

Daphnia magna: 48 hr  $10_{B0} = 0.41 \text{ mg/l} (.37 - .49 \text{ T.L.})$ Fathead minnow: 96 hr  $10_{50} = 2.9 \text{ mg/l} (2.5 - 3.3 \text{ T.L.})$ Bluegill Sunfish: 96 hr  $10_{50} = 4.3 \text{ mg/l} (4.2 - 6.6 \text{ T.L.})$ Rainbow trout: 96 hr  $10_{50} = 14.7 \text{ mg/l} (10 + 15.5 \text{ T.L.})$ 

The above LC, values represent toxicity levels for the next formulation when 100% of the "free" actives are available to the aquatic organism (that is, no suspended solids for adsorption of the actives).

However, when the formulation is exposed to adsorbent material (i.e., bentonite clay or activated carbon), acute toxicity is greatly reduced due to the adsorption properties of the active ingredients. Tables 1 to 4 provide cumulative percent mortalities to fathead minnow and <u>Daphnia mains of Clam-Trol CT-1</u> which has been exposed to various concentrations of either bentonite clay or activated carbon. Even the most sensitive test species, <u>Daphnia macma</u>, was not affected when sufficient tay or carbon was available to adsorb the free actives. A sufficient to 1 of clay to Clam-Trol CT-1 and 2 to 1 of activated carbon to Clam-Trol CT-1 resulted in the reduction of acute toxicity to fathead minnows to the point that the water becomes essentially

Both the LC bloassays and the detoxification studies were conducted by the Aquatic Texicology Laboratory of Betz Laboratories. conversion after a two week acclimation period. It was concluded from this study that biodegradation of the Quat was, after a short period of microbial acclimation, quite rapid and complete.

Biodegradation of DGH was examined in 1989 using the CECD Screening Test according to EC Directive 79/831. For the OECD study, a DGH solution was diluted with nutritive salt solutions and mud from the biological part of a clarification plant to nearly 40 mg/l DOC in water. The system was shaken at 24 °C in the dark for 28 days. Dissolved Organic Carbon (DOC) determinations were used to monitor biodegradability of the DGH compound. Test results are presented in the table below.

#### Biodegradation of DGH (OECD Protocol)

Day	DOC mg/l	% Degradation
0	3.4	
1	39	0
4	2.6	33
7	2.6	3.3
14	17	56
18	16	59
22	18	54
26	13	67
29	10	74
31	9	77
10 M		

The DGH exhibited a DOC removal of greater than 70% within 28 days enabling it to be reported as "easily biodegradable" according to the test standard.

In another study (Goldberg, M.C., et.al., 1969), dodecylguanidine acetate (DGA), an agricultural fungicide, was investigated to evaluate the biodegradation potential by microorganisms originating from soil and river muds. Two species of soil bacteria, one an aerobe and another an anaerobe that were isolated on agar plates and then transferred to dodine (DGA) salt media, grew profusely after a 7 day lag period. When these bacterial species were transferred back to a dodine-free medium, growth of the organisms was poor. This study provided a demonstration that certain organisms were quite capable of utilitzing DGA as the sole source of carbon.

#### Ricacoumulation

Dioaccumulation studies (Rohm and Haas study) with bluegill sunfigh determined the steady state interval, which is the time when absorption equals elimination using "C labelled Quat. The steady state interval occurred in the fish after 2 weeks of continuous exposure at sublethal levels at which time the carbon 14 residues in the carcass and the viscera reached a plateau. The concentration of the biocide in the carcass of the fish at the steady state was 42 times that of the concentration of water. It was also found that the biological half-life of the accumulated residues was short, about 7 days, which was determined by the elimination of the carbon 14 residues when the fish were placed in a biocide-free aguarium.

#### Summary:

The biocidal activity of Clam-Trol CT-1 results from the two cationic surface active agents (DGH and Quat) in this formulation. The product's efficacy is based on its ability to alter or disrupt various membrane systems of the biofouling organisms. These same inherent properties of these agents which provide biocidal efficacy are rapidly neutralized upon adsorption to many types of naturally occurring materials thus reducing or eliminating acute toxicity to non target organisms.

Several key characteristics of Clam-Trol CT-1 will minimize its environmental impact following its application to cooling systems. These include:

- Adsorption rates of both actives are rapid and thus biocidal activity is short-lived. Both actives readily adsorb to suspended material, sediments, and the surfaces within a cooling system.
- Both of the active components in the formulation are readily biodegradable. Solutions of Quat have been shown to biodegrade by more than 90% in 2 days while solutions of DGH exhibited 70% biodegration in 28 days.
- Clam-Trol CT-1 provides an alternative to chlorine or a number of halogenated organic or metal containing blocides that are considerably less environmentally desirable.
- Bioaccumulation of the Quat active has been determined by continuous exposure of low levels of free actives to fish, as reaching a steady state after 2 weeks. The half-life of this accumulated material is short once exposure ceases.
- An analytical field method is available for determining the presence of the actives in a treated cooling system. The method is also useful for monitoring discharges.

Biofouling treatment programs to cooling systems need to employ innovative technology that will direct the applications in a most effective manner to the target organisms. Applications of Clam-Trol CT-1 can serve to protect cooling systems from both macrofouling and microfouling problems using state-of-the-art technology. No other treatment program exists that can protect a system from infestation by adult mollusks and larvae by employing seasonal applications. Effective control and protection can be accomplished within a 24 hour application. In addition, Clam-Trol CT-1 applications can provide microfouling protection to safety-related cooling systems due to its unique fast-acting properties and its ability to permeate slime formations. These are applications that will not cause the corrosive problems that develop from continuous chlorination nor require extensive treatment periods for control.

# analytical data

## CLAM-TROL® CT-1 METHYL ORANGE METHOD

#### APPARATUS REQUIRED

a

Beaker, glass, 50 mL (2 required) C	ode **
Cylinder, graduated, 25 mL	2622
Funnel Rack, separatory	936
Funnel, separatory, with a Teflon stopco (2 required)	ock, 250 mL **
Glass Rod	114
Optical Cell, (2 required)	**
Spectrophotometer	**
GENERAL APPARATUS *	
Cylinder, graduated, 100 mL	Code 121
Cylinder, graduated, 250 mL	917
Flask, volumetric, 1 L, glass (4 required	d) 935
Pipet, glass, graduated, 1 mL	140
Pipet, glass, volumetric, 1 mL	866
Pipet, glass, volumetric, 3 mL	**
Pipet, glass, volumetric, 5 mL	124
Pipet, glass, volumetric, 10 mL	123
Pipet, glass, volumetric, 15 mL	861
Pipet, glass, volumetric, 20 mL	**
Pipet, glars, volumetric, 25 mL	. 117
Pipet, glass, volumetric, 30 mL	**

\* The general apparatus required for the test is determined by the specific test procedure used.

\*\* Apparatus not available through Betz Lab Supply should be obtained through a local supplier.

#### CHEMICALS REQUIRED

1, 2 - Dichloroethane (reagent) Code 1668 grade or equivalent)

CT-1 Buffer Reagent	1591
Methanol (reagent grade or equivalent)	322
Drying Reagent, with a plastic dipper	1271

#### SUMMARY OF METHOD

In this procedure the dye in the CT-1 Buffer Reagent complexes with the active ingredients in Clam-Trol CT-1. This complex is extracted into 1, 2 - dichloroethane. The organic layer containing the complex is separated from the aqueous layer and dried with a drying reagent containing anhydrous sodium sulfate. The color intensity of the 1, 2 dichloroethane layer is then measured in a spectrophotometer at 415 nm.

This method must be customized to each specific application. Vary the volumes of sample, CT-1 Buffer Reagent, and 1, 2 - dichloroethane according to the test range (see Table 1). If a higher absorbance is needed, increase the volume of sample or decrease the volume of 1, 2 dichloroethane. When increasing the sample volume it may be necessary to increase the volume of CT-1 Buffer Reagent used. For samples < 150 mL use 10 mL of CT-1 Buffer Reagent; for samples between 150 and 300 mL use 15 mL of CT-1 Buffer Reagent. Make sure that enough 1, 2 - dichloroethane is used to leave a small plug of solvent in the separatory funnel when the bottom layer of solvent is removed and to fill the optical cell property.

#### GENERAL PROCEDURE

#### Use a well-ventilated or hooded area to run the test. Atways use a safety bulb when pipetting liquids.

1,2 - Dichloroethane (also known as Ethylene Dichloride) is a priority pollutant and a specifically-listed RCRA-regulated material subject to specific disposal restrictions and/or prohibitions. For this reason, all used 1,2 - dichloroethane should be segregated from other waste streams. Dispose of waste 1,2 - dichloroethane in an approved manner (e.g., labpacking or incineration).

Range CT-1 (mg/L)	Volume CT-1 Buffer (mL)	Volume Dichloroethane (mL)	Volume Sample (mL)	Optical Cell Size
0.2 - 3.0	15	10	8 250	1.0 cm *
1.0 - 25.0	10	30	50	2.5 cm **
0.2 - 1.0	15	20	200	5.0 cm ***

#### Table 1. Suggested Volumes for Various Ranges of CT-1

\* The1.0-cm cell (Code 1312) can be used with Hach spectrophotometers using a 1-cm cell adapter (Code 2776C).

\*\* The 2.5-cm cell is the standard Hach 1-in. cell (Betz Code 2601).

\*\*\* Five centimeter cells are not available for use with the Hach photometers. Many laboratory spectrophotometers require an adapter to accommodate 5-cm cells. Check with the instrument manufacturer.

- Transfer an aliquot of the water sample to a separatory funnel (the sample). Transfer the same volume of distilled (or deionized) water to a second separatory funnel (the blank). Run the blank once for each set of samples tested (see Notes 1, 2, and 3).
- Add CT-1 Buffer Reagent to both the sample and the blank.
- Using a pipet, add 1, 2 dichloroethane to both separatory funnels.
- Insert the stoppers in each of the separatory funnels. Invert and briefly open the stopcock to vent the funnels (see Notes 4 and 5). When venting the funnels, point the tip of the funnel away from yourself and others.
- Shake the funnels moderately for 30 sec, vent the funnels, then allow them to stand for 10 min (but no longer than 15 min).
- Collect the lower layer (1, 2 dichloroethane) from each funnel in 50-mL beakers leaving about 1-2 mL in the funnel. This will prevent significant removal of water.
- Using the plastic dipper, add 2 scoops of Drying Reagent to each beaker and stir with a glass rod for 15 sec (but no longer than 30 sec).
- Walt approximately 1 to 2 min (but not more than 5 min). Then carefully decant the extract off of the drying reagent into an optical cell.
- Set the spectrophotometer at 415 nm and zero with 1, 2 - dichloroethane. Measure and record the absorbance of the blank and the sample (see Note 6).
- The sample absorbance minus the blank absorbance is used to determine the concentration of CT-1 in the sample. From a prepared calibration curve, determine the CT-1 concentration in the sample (see Calibration Curve Preparation).
- Clean the cells after each measurement (see Note 7).

#### CALIBRATION CURVE PREPARATION

- Prepare a 1000 mg/L CT-1 stock solution by accul rately weighing 1.00 g of CT-1 into 1 L of distilled (or deionized) water.
- Pipet designated volumes of the stock solution into 1-L volumetric flasks. These are the standard solutions used in preparing a calibration curve. Use Table 2 to make appropriate dilutions of the stock solution for each specific application.
- 3. Follow the General Procedure using the specific solution volumes that have been determined for the application and prepare a calibration curve. Determine the absorbance of a blank solution using distilled (or deionized) water. This blank can be subtracted from the sample absorbance or used to zero the spectrophotometer so that the calibration curve goes through the origin. The calibration curve should be linear over the indicated ranges.

#### NOTES

- For maximum accuracy the calibration curve should be checked by every operator using this test and should be verified a minimum of twice per month using a freshly prepared CT-1 standard.
- A blank measurement must be recorded for each set of samples. The blank reading may vary slightly; however, the absolute difference between the sample and the blank remains relatively constant.
- Chlorine causes a negative interference in the test. This can be eliminated by adding 0.1 N Sodium Thiosultate (Code 235) to the water sample before running the test. The amount added be is based on the concentration of chlorine in the system. For a 100-mL water sample containing 0.3 mg/L chlorine, add 10 drops of 0.1 N Sodium Thiosultate to remove the interference.

of 1 L.	
Concentration CT-1 Desired (mg/L)	CT-1 Stock Solu- tion Added to Make 1 L (mL)
0.2	0.2
0.4	0.4
0.6	0.6
0.8	0.8
1.0	1.0
5.0	5.0
10.0	10.0
15.0	15.0
20.0	20.0
25.0	25.0

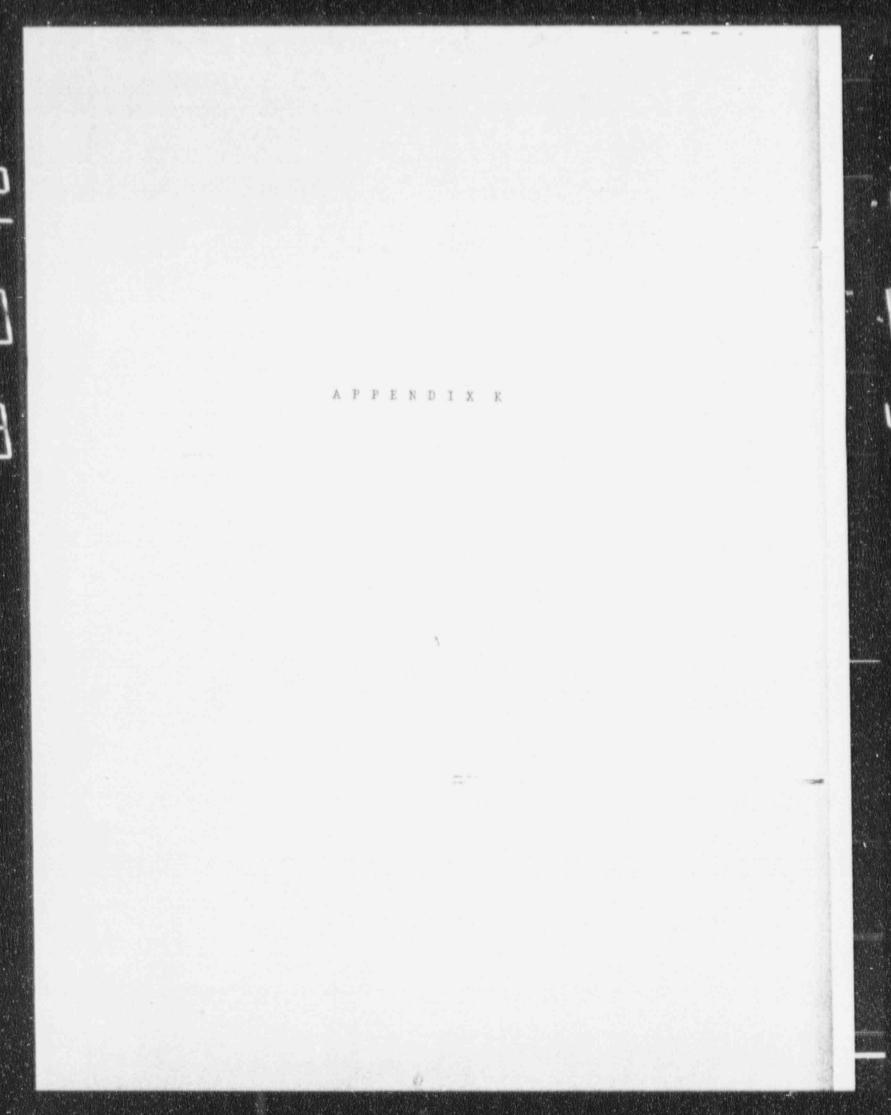
Table 2. Dilutions for Calibration Curve Preparation Based on a Final Solution Volume

 A slight emulsion may form when using natural water samples. When this happens, vary step 5 of the procedure. Shake the funnel for 30 sec, vent it, then allow it to stand for 5 min. Gently invert the funnel once then allow the funnel to stand for 5 min.

 It is important to vent the separatory funnel both before and after shaking it. Otherwise, a pressure will build up in the funnel that can cause the stopper to be forced out of the top of the funnel.

-6

- Use caution when inserting or removing the sample cell in the photometer. The 1, 2 - dichloroethane can damage the cell compartment.
- It is imperative that the sample cells are kept clean during the running of the test. It is recommended that the cells are cleaned after each measurement using the following procedure:
  - a) Rinse the cell three times with distilled (or deionized) water.
  - b) Rinse the cell three times with methanol.
  - c) Rinse the cell three times with 1, 2 dichloroethane to remove methanol from the cell.
- This method is based upon Wang, L. K.; Langly, D. F. Ind. Eng. Chem., Prod. Res. Dev., 1975, 14, 3, 210-212.



#### BETZ LABORATORIES, INC. 4636 SOMERTON ROAD, TREVOSE, PA. 19047 BETZ MATERIAL SAFETY DATA SHEET 24 HOUR EMERGENCY TELEPHONE (HEALTH OR ACCIDENT) 215/355-3300

PRODUCT : CLAM-TROL CT-1

(PAGE 1 OF 3) EFFECTIVE DATE 05-18-89 PRINTED: 3-Sep-1989 REV:SEC.3

PRODUCT APPLICATION : WATER-BASED MICROBIAL CONTROL AGENT. ----SECTION 1-----HAZARDOUS INGREDIENTS-----INFORMATION ON PHYSICAL HAZARDS, HEALTH HAZARDS, PEL'S AND TLV'S FOR SPECIFIC PRODUCT INGREDIENTS AS REQUIRED BY THE OSHA HAZARD COMMUNICATIONS STANDARD IS LISTED. REFER TO SECTION 4 (PAGE 2) FOR OUR ASSESSMENT OF THE POTENTIAL ACUTE AND CHRONIC HAZARDS OF THIS FORMULATION.

ETHYLENE GLYCOL\*\*\*CAS#107-21-1;LIVER, KIDNEY AND BLOOD TOXIN;CNS DEPRESSANT; ANIMAL TERATOGEN (HIGH ORAL DOSES) ; PEL/TLV: 50PPM-C.

ALKYL DIMETHYL BENZYL AMMONIUM CHLORIDE\*\*\*CAS#68424-85-1; CORROSIVE(EYES) ; FEL:NONE; TLV:NONE.

ISOPROPYL ALCOHOL \*\*\* (IPA) ; CAS #67-63-0; FLAMMABLE LIQUID; CHRONIC OVEREXPOSURE MAY CAUSE LIVER AND KIDNEY TOXICITY; PEL/TLV:400PPM(500PPM-STEL). DODECYLGUANIDINE HYDROCHLORIDE\*\*\* (DGH) ; CAS#13590-97-1; CORROSIVE ; PEL: NONE ; TLV:NONF.

ETHYL ALCOHOL\*\*\* (ETHANOL) ; CAS#64-17-5; FLAMMABLE; MAY CAUSE DEFATTING DERMATITIS, DIZZINESS AND HEADACHE; PEL: 1000FFM; TLV: 1000FFM.

----SECTION 2-----TYPICAL PHYSICAL DATA-----

(APPROX.) 5.3 ODOR: MILD PH: AS IS FL. PT. (DEG.F): 116 SETA(CC) SP.GR. (70F)OR DENSITY: 1.022 VAPOR PRESSURE(mmHG): 23 VISC cDs70F: 23 VISC cps70F: 23 EVAP.RATE: <1 ETHER=1 PHYSICAL STATE: LIQUID

VAPOR DENSITY (AIR=1): >1 \$SOLUBILITY (WATER): 100 APPEARANCE: COLORLESS FREEZE POINT(DEG.F): <-30

----SECTION 3----REACTIVITY DATA------

STABLE, MAY REACT WITH STRONG OXIDIZERS, DO NOT CONTAMINATE, BETZ TANK CLEAN-OUT CATEGORY 'B'

THERMAL DECOMPOSITION (DESTRUCTIVE FIRES) YIELDS ELEMENTAL OXIDES.

BETZ MATERIAL SAFETY DATA SHEET (PAGE 2 OF 3) EFFECTIVE DATE 05-18-8! PRODUCT: CLAM-TROL CT-1 ----SECTION 4----HEALTH HAZARD EFFECTS----the size was any one day, and any and and any and the day of any ACUTE SKIN EFFECTS \*\*\* PRIMARY ROUTE OF EXPOSURE CORROSIVE TO SKIN. POTENTIAL SKIN SENSITIZER ACUTE EYE EFFECTS \*\*\* CORROSIVE TO THE EYES ACUTE RESPIRATORY EFFECTS \*\*\* PRIMARY ROUTE OF EXPOSURE VAPORS, GASES, MISTS AND/OR AEROSOLS CAUSE IRRITATION TO UPPER RESPIRATORY TRACT CHRONIC LIFECTS OF OVEREXPOSURE\*\*\* PROLONGED OR REPEATED OVEREXPOSURES MAY CAUSE: TISSUE NECROSIS; BLOOD CELL DAMAGE OR IMPAIR BLOOD CELL FUNCTION; REPRODUCTIVE SYSTEM TOXICITY; SKIN SENSITIZATION. MEDICAL CONDITIONS AGGRAVATED \*\*\* NOT KNOWN SYMPTOMS OF EXPOSURE \*\*\* INHALATION OF VAPORS/MISTS/AEROSOLS MAY CAUSE EYE, NOSE, THROAT AND LUNG IRRITATION ; SKIN CONTACT MAY CAUSE SEVERE IRRITATION OR BURNS . PRECAUTIONARY STATEMENT BASED ON TESTING RESULTS \*\*\* MAY BE TOXIC IF ORALLY INGESTED. ----SECTION 5-----FIRST AID INSTRUCTIONS------SKIN CONTACT\*\*\* REMOVE CLOTHING. WASH AREA WITH LARGE AMOUNTS OF SOAP SOLUTION WATER FOR 15 MIN. IMMEDIATELY CONTACT PHYSICIAN EYE CONTACT \*\*\* IMMEDIATELY FLUSH EYES WITH WATER FOR 15 MINUTES. IMMEDIATELY CONTACT A PHYSICIAN FOR ADDITIONAL TREATMENT INHALATION EXPOSURE\*\*\* REMOVE VICTIM FROM CONTAMINATED AREA. APPLY NECESSARY FIRST AID TREATMENT. IMMEDIATELY CONTACT & PHYSICIAN. INGESTION\*\*\* DO NOT FEED ANYTHING BY MOUTH TO AN UNCONSCIOUS OR CONVULSIVE VICTIM DO NOT INDUCE VOMITING. IMMED. CONTACT PHYSICIAN. DILUTE CONTENTS OF STOMACH USING 3-4 GLASSES MILK OR WATER ----SECTION 6-----SPILL, DISPOSAL AND FIRE INSTRUCTIONS-----SFILL INSTRUCTIONS\*\*\* VENTILATE AREA, USE SPECIFIED PROTECTIVE EQUIPMENT. CONTAIN AND ABSORB ON ABSORBENT MATERIAL, PLACE IN WASTE DISPOSAL CONTAINER. THE CONTAMINATED ABSORBENT SHOULD BE CONSIDERED A PESTICIDE AND DISPOSED OF IN AN APPROVED PESTICIDE LANDFILL.SEE PRODUCT LABEL STORAGE AND DISPOSAL INSTRUCTIONS. REMOVE IGNITION SOURCES.FLUSH AREA WITH WATER.SPREAD SAND/GRIT. DISPOSAL INSTRUCTIONS\*\*\* WATER CONTAMINATED WITH THIS PRODUCT MAY BE SENT TO A SANITARY SEWER TREATMENT FACILITY, IN ACCORDANCE WITH ANY LOCAL AGREEMENT, A PERMITTED WASTE TREATMENT FACILITY OR DISCHARGED UNDER A NPDES PERMIT PRODUCT(AS IS) -DISPOSE OF IN APPROVED PESTICIDE FACILITY OR ACCORDING TO LABEL INSTRUCTIONS FIRE EXTINGUISHING INSTRUCTIONS\*\*\* FIREFIGHTERS SHOULD WEAR POSITIVE PRESSURE SELF-CONTAINED BREATHING APPARATUS (FULL FACE-PIECE TYPE). DRY CHEMICAL, CARBON DIOXIDE, FOAM OR WATER

BETZ MATERIAL SAFETY DATA SHEET (FAGE 3 OF 3)

PRODUCT: CLAM-TROL CT-1 EFFECTIVE DATE 05-18-8 USE PROTECTIVE EQUIPMENT IN ACCORDANCE WITH 29CFR SECTION 1910.132-134. USE

RESPIRATORS WITHIN USE LIMITATIONS OR ELSE USE SUPPLIED AIR RESPIRATORS. VENTILATION PROTECTION\*\*\*

ADEQUATE VENTILATION TO MAINTAIN AIR CONTAMINANTS BELOW EXPOSURE LIMITS RECOMMENDED RESPIRATORY PROTECTION\*\*\*

IF VENTILATION IS INADEQUATE OR SIGNIFICANT PRODUCT EXPOSURE IS LIKELY, USE A RESPIRATOR WITH ORGANIC VAFOR CARTRIDGE & DUST/MIST PREFILTER RECOMMENDED SKIN PROTECTION \*\*\*

GAUNTLET-TYPE RUBBER GLOVES, CHEMICAL RESISTANT APRON

WASH OFF AFTER EACH USE. REPLACE AS NECESSARY

RECOMMENDED EYE PROTECTION\*\*\*

SPLASH PROOF CHEMICAL GOGGLES.FACE SHIELD

STORAGE INSTRUCTIONS\*\*\*

KEEP DRUMS & PAILS CLOSED WHEN NOT IN USE.

STORE IN COOL VENTILATED LOCATION.STORE AWAY FROM OXIDIZERS MANDLING INSTRUCTIONS\*\*\*

GENERAL-IMMEDIATELY REMOVE CONTAMINATED CLOTHING, WASH BEFORE REUSE

SPECIFIC- COMBUSTIBLE. GO NOT USE AROUND SPARKS OR FLAMES. BOND CONTAINERS DURING FILLING OR DISCHARGE WHEN PERFORMED AT TEMPERATURES AT OR ABOVE THE PRODUCT FLASH FOINT.

THIS MSDS COMPLIES WITH THE OSHA HAZARD COMMUNICATION STANDARD HAROLD M. HERSH (ENVIRONMENTAL INFORMATION COORDINATOR)

THE CONTENT OF THIS APPENDIX REPRESENTS INFORMATION KNOWN TO BETZ ON THE EFFECTIVE DATE OF THIS MSDS. THIS INFORMATION IS BELIEVED TO BE ACCURATE. ANY CHANGES IN REGULATIONS WILL RESULT IN UPDATED VERSIONS OF THIS DOCUMENT.

...TSCA: ALL COMPONENTS OF THIS PRODUCT ARE LISTED IN THE TSCA INVENTORY ...FIFRA(40CFR):EPA REG.NO. 3876- 145 ...REPORTABLE QUANTITY(RQ) FOR UNDILUTED PRODUCT: NOT APPLICABLE ...RCRA: IF THIS PRODUCT IS DISCARDED AS A WASTE,THE RCRA HAZARDOUS WASTE IDENTIFICATION NUMBER IS: DOO1=IGNITABLE;D002=CORROSIVE ...DOT HAZARD CLASSIFICATION: CORROSIVE TO SKIN.COMBUSTIBLE

... DOT SHIPPING DESIGNATION IS: UN1760 CORROSIVE LIQUID, N.O.S.

...THIS PRODUCT CONTAINS THESE CHEMICALS KNOWN TO THE STATE OF CALIFORNIA TO CAUSE CANCER OR REPRODUCTIVE TOXICITY: NONE PRESENT IN SIGNIFICANT AMOUNTS ...SARA SECTION 302 CHEMICALS: NONE PRESENT IN SIGNIFICANT AMOUNTS ...SARA SECTION 313 CHEMICALS: ETHYLENE GLYCOL(107-21-1) , 21.0-30.0% ; ...SARA SECTION 312 HAZARD CLASS: IMMEDIATE(ACUTE), DELAYED(CHRONIC) AND FIRE ...MICHIGAN CRITICAL MATERIALS: NONE PRESENT IN SIGNIFICANT AMOUNTS NFFA/HMIS : HEALTH - 3 ; FIRE - 2 ; REACTIVITY - 0 ; SPECIAL - CORR ; PE - D

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## Clam-tro THESE ENGINES ACENT

USE DIRECTIONS CONTINUED FROM FOREL ONE ONCE-THROUGH

INDUSTRIAL COOLING WATER SYSTEMS

This product aids in the control of melleres and of signf. Socterial and fangal climps in excethrough and classed-reprise frack and non-matter canling systems, couling gands, cousis, and inguous, this product may be added to the against inist mater or before any contemizated area in the againm. Addition of this product should be node with a wetering pamp: it may be continuous or intermittent depending open the coverity of contomination when treatment is began, and the retention time in the tetten.

REALY FORED SYSTEMS went be cleaned before trantmost is begon

#### FOR THE COMING. OF MOLLINSCA, RACIERIA, FUNCI AND ALCOF

#### INTERMITTENT ON SLIE METHOD

INITIAL 2005: When the agetem is mellicably familed, add this predect at the rate of 0.2 to 1 0 pound (24 to 120 ypm) per 1000 gallens of water based on the Flow rate through the option. Minimum treatment Intervals should be 15 minutus. Repeat until control is achieved.

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AUXIL TORY HOTER

AND HASTE WATER SYSTEMS

This product way be added to the system by slap or intermitteel food or by spraping onto a matte pile. The frequency of feed or opray and the doration of irestment will depend upon the severity of the contamination ddditions to water excluse should be made during the pemping aperation and at close to the news or percipie to second plaquate mining.

#### THIS PHILITENT OF SLOS HETWOO

When broatment is required, add this predect at the rate of 1.5 to 4.0 younds per 1000 gallans of nator alrendy in the restam, or being added to the system. For 4 to 8 hours, 1 to 4 times per weel or as needed to achieve the desired level of control [ Men control ]; abtained, add this product at the rais of 0.75 to 2.0 pounds per 1800 molions of usion in the system.

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SHY LO SHOW TO ST MERIC	CONTRACT OF CASE OF	12 100	10	1	

## TREVOSE, PR 19047 BUSINESS PHONE: 215-355-3200 EMERGENCY(HEALTH OR ACCIDENT): 215-355-3300

