CALSPAN ADVANCED TECHNOLOGY CENTER

MITIGATION OF BIOFOULING USING COATINGS

QUARTERLY PROGRESS REPORT #3

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DISCLAIMER

Objectives

Objectives of this project are to evaluate benefits associated with control of the surface energetic properties of materials used in heat exchangers; and to identify preferred ranges of these surface conditions that minimize deposits of biological fouling known to deteriorate heat exchange efficiencies in seawater, brackish water and freshwater systems. The technical approach employed uses special diagnostic plates in novel flow cells where fluid flow conditions can be well-controlled, modifying the surface chemistry and surface energy of the plates with very thin coatings and examining the earliest events of biofouling caused by macromolecules and microbial organisms.

Project Activity - March to June 1981

Exposure Experiments

The complete series of flow cell exposure tests were initiated during this period. A total of 40 flow cells, containing two test plates each, will be exposed before the task is completed (Figure 1). The 40 cells are divided into 5 sets of 8 cells each. The test regimen includes 5 surface types, 4 exposure times each, and duplicates. The experimental time plan (Table 1) is designed to minimize any effects of slight variations in the barnacle tank system. The plan requires, however, that any firm conclusions from the acquired data will be postponed until all of the plates are analyzed.

The flow cell parameters were outlined in Quarterly Progress Report Number 2 (March 16, 1981). All of the experiments will be carried out during the 14 hours daylight/10 hours dark cycle. The chemical characteristics of the tank water are being analyzed every three weeks during this period. The water temperature has averaged 80 $\pm$ 2°F and the specific gravity has averaged 1.026 $\pm$ .001 g/ml since the beginning of the flow cell tests in May.

Set I of the experiments is complete. Set II will be completed as soon as the scanning electron microscopy and energy-dispersive x-ray analyses are finished. The preliminary results for Sets I and II are given in this report. Set III is being exposed at this writing and Sets IV and V will be completed by July 24.

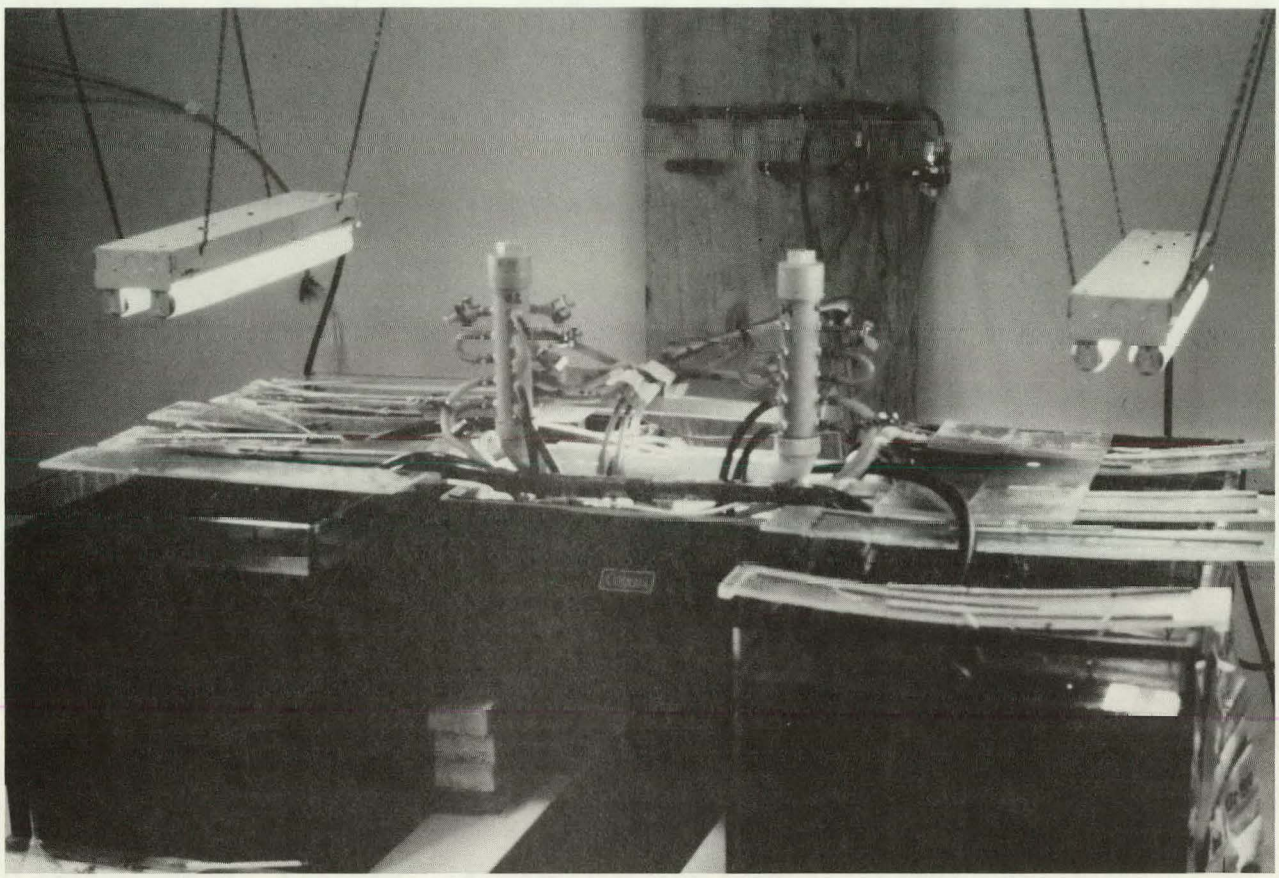


Figure 1 PHOTO OF THE BARNACLE TANK/FLOW CELL SYSTEM. TWO FLOW CELLS WERE BEING EXPOSED TO THE SEAWATER WHEN THE PHOTO WAS TAKEN. THE SCRUBBER TANK AND MANIFOLD SYSTEM ARE SEEN IN THE AREA BETWEEN THE TWO 50-GALLON AQUARIA.

Table 1
TANK EXPLOSURE PLAN

PLATE TREATMENT	# DAYS EXPOSURE	SET #				
		I	II	III	IV	V
RADIO FREQUENCY GLOW DISCHARGE	1	●		●		
	3			●		●
	6		●			●
	12		●		●	
DETERGENT WASH	1	●			●	
	3	●		●		
	6			●		●
	12	●				●
CHLOROPROPYLTRI-CHLOROSILANE COATING	1		●		●	
	3	●			●	
	6	●		●		
	12			●		●
DIMETHYLDI-CHLOROSILANE COATING	1		●			●
	3		●		●	
	6	●			●	
	12	●		●		
HEPTAFLUOR-- COATING	1			●		●
	3		●			●
	6		●		●	
	12		●		●	

Sets I and II - Results

The average results and standard deviations for the first two sets of flow cells are given in Table 2. Data for each parameter are acquired by the following methods and for the following reasons:

Thickness - The raw data are obtained using an ellipsometer and the coating thickness is calculated with the aid of a National Bureau of Standards (NBS) computer program. The calculated values are, first, the optical thicknesses of the coatings (pre-exposure and post-exposure) on the test plate; further resolved into geometric thickness and refractive index terms by the NBS program. Subtraction of the pre-exposure value from the post-exposure value results in the thickness of the adsorbed biofouling film. Data are taken at two specific areas for each test plate; i.e., 4 areas per test cell.

Infrared Absorbance - is measured for each prism; i.e., 2 measurements per test cell. The purpose of obtaining the IR spectrum is to determine the chemical nature of the adsorbed fouling film. Proteins, esters, and carbohydrates are of particular interest to the study of biofouling. Determining the ratio of certain bands within a spectrum is a means to determine slight changes in the composition of the adsorbed material.

Contact Potential - is measured for each prism in each test cell. The value is given in millivolt units and represents the electrical "potential" (related to classical "work function") of the surface. Measuring the contact potential after exposure results in ascertaining the potential of the entire substrate/adsorbed layer "battery;" subtracting the pre- and post-exposure values gives the potential of the adsorbed film. High positive values usually indicate increasing amounts of adsorbed organic contaminants.

Critical Surface Tension (γc) - is determined from contact angle data plots for one plate per test cell. The calculated γ_c is an indication of the surface energy of the surface. The slope of the plotted data is a function of the degree of polarity of the surface.

Table 2

PRELIMINARY DATA FROM TANK EXPOSURE EXPERIMENTS (SETS I, II)

PLATE TREATMENT	# DAYS EXPOSURE	PRE-EXPOSURE			POST-EXPOSURE			DELTA (THE ADSORBED FILM)					
										IR ABSORBANCE			
		γ_c* (cynes/cm)	COATING THICKNESS (Angstroms)	COATING POTENTIAL (millivolts)	γ_c	COATING THICKNESS	CONTACT POTENTIAL	COATING THICKNESS	CONTACT POTENTIAL	AMIDE I	AMIDE II	I/II	#BACTERIA/cm^2** (x10^5)
RADIO FREQUENCY GLOW DISCHARGE	1	>50	–	~100+	39.4	161± 9	694± 13	161± 9	594 ± 9	0.062 ± 0.016	0.49 ± 0.011	1.27± 0.01	44.7± 4.6
	3		–			•							
	6		–		38.7	741 ± 29	606 ± 39	741 ± 29	506 ± 39	0.143	0.092	1.55	••
	12		–		35.1	745 ± 26	560 ± 30	745 ± 26	460 ± 30				••
DETERGENT WASH	1	32.0	–	79 ±136	40.6	148 ±15	686 ± 20	148 ± 15	608 ± 116	0.054 ± 0.004	0.043± 0.004	1.26 ± 0.03	94.2 ± 70.0
	3		–	52 ±136	40.5	526 ±44	587 ± 7	526 ± 44	535 ± 143	0.091 ± 0.001	0.068± 0.008	1.36 ± 0.015	104 ± 6.8
	6		–										
	12		–	82 ±23	39.9	968 ± 54	532 ± 17	968 ± 54	450 ± 6	0.182 ± 0.030	0.126± 0.008	1.44 ± 0.14	78.3 ± 6.8
CHLOROPROPYL... COATING	1	32.0	391 ± 67	217 ±110	30.5	552 ± 57	490 ±41	161 ± 63	273 ± 69	0.041 ± 0.008	0.010± 0.001	4.05± 0.77	••
	3		210 ±26	-46 ± 45	30.8	470 ±31	395 ± 31	260 ± 45	441 ± 76	0.048 ± 0.001	0.034± 0.008	1.47 ± 0.34	71.9 ± 38.4
	6		169 ± 19	170 ± 6	34.0	516 ± 102	428 ± 50	348 ± 120	258 ± 44	0.080 ± 0.024	0.072± 0.012	1.10 ± 0.015	117 ± 33.9
	12												
DIMETHYL... COATING	1	21.6	63 ±25	392 ± 6	24.3	371 ± 14	710 ± 32	300 ± 28	318 ± 38	0.046 ± 0.007	0.18 ± 0.004	2.72 ± 0.95	••
	3		66 ±20	388 ±20	25.0	585 ± 68	625 ± 5	519 ± 65	237 ± 16	0.080 ± 0.016	0.038± 0.004	2.13 ± 0.66	••
	6		80 ± 8	207 ± 1	25.5	753 ± 67	662 ± 1	674 ± 45	455 ± 1	0.089 ± 0.001	0.067± 0.001	1.33± 0.04	70.3 ± 22.4
	12		74 ± 21	162 ± 1	22.7	537 ± 102	642 ± 64	463 ± 112	480 ± 64	0.065 ± 0.004	0.035± 0.007	1.88 ± 0.26	25.5 ± 4.5
HEPTAFLUOR... COATING	1	19.0											
	3		56 ± 15	281 ± 5	30.0	878 ± 37	271 ± 47	822 ± 42	552 ± 52	0.049 ± 0.008	0.016± 0.004	3.10 ± 0.30	••
	6		40 ± 11	250 ± 19	30.0	696 ± 55	179 ± 55	656 ± 55	429 ± 74	0.053± 0.010	0.024± 0.006	2.18 ± 0.16	••
	12		40 ± 11	296 ± 14	31.0	681 ± 108	192 ± 3	640 ±108	488 ± 15				••

* γ_c: CRITICAL SURFACE TENSION; PRE-EXPOSURE VALUES ASSUMED FROM THOSE CALCULATED IN COATING VIABILITY TESTS.

**#BACTERIA/cm^2: CALCULATED FROM # COUNTED IN SEM PHOTOMICROGRAPHS THAT WERE TAKEN AT 5000X MAGNIFICATION; SEM DATA FROM SET I ONLY AT THIS TIME.

+ CONTACT POTENTIAL OF RFGDT'D PLATES NOT MEASURED PRE-EXPOSURE DUE TO HIGH SURFACE ACTIVITY OF THE SURFACES; ESTIMATED TO BE APPROXIMATELY 100 MILLIVOLTS FROM PRIOR EXPERIENCE.

SEM/EDX-ray - analyses are carried out on 2 areas of one plate per test cell. Photomicrographs are recorded at 50X, 500X, and 5000X and show adsorbed films and bacteria. The EDX-ray analysis is a means to determine the elemental composition (sodium and above) of the surface layer.

Preliminary conclusions that can be drawn from the data for each surface are:

(1) An organic fouling film is adsorbed on all the test surfaces within one day of tank water exposure.

(2) The contact potentials of the surfaces increase by several hundred millivolts as the organic film is adsorbed.

(3) The critical surface tensions of the surfaces change to different degrees during exposure.

(4) The adsorbed film contains proteinaceous material and cellulosics (Figure 2).

(5) Bacteria dwell on the surfaces within 3 days of exposure (Figure 3).

The sharp bands in Figure 2 were determined to be representative of natural cellulosic materials only after an infrared spectral study of the man-made components of the tank/cell system (pump material, tubings, sealants, etc.) was conducted. Likely sources for the adsorbed cellulosic polymers are algal and other biological exudates into the aquaria seawater from the thriving living populations of maritime organisms harbored therein. Alternative sources are biodegradation and oxidation products of the "woody" brine shrimp egg shells added to the tank system, and/or similar bioproducts of polyphenolic composition. It is important to note that these adsorbed products also were found in our earlier experiments in natural seawater at Key West, Florida.

Only the dimethyldichlosilane coating retained a critical surface tension (γ_c) that was in the "nonbioadhesive" range (20-30 dynes/cm) throughout the 12-day exposure period. The term "nonbioadhesive" does not mean that the surface will remain completely free of fouling, but that microfouling will be only loosely adsorbed and will tend to slough under normal flow conditions. The thickness and bacteria density data in Table 2 and the SEM photomicrographs in Figure 4 support this view. The films adsorbed on the other surfaces,

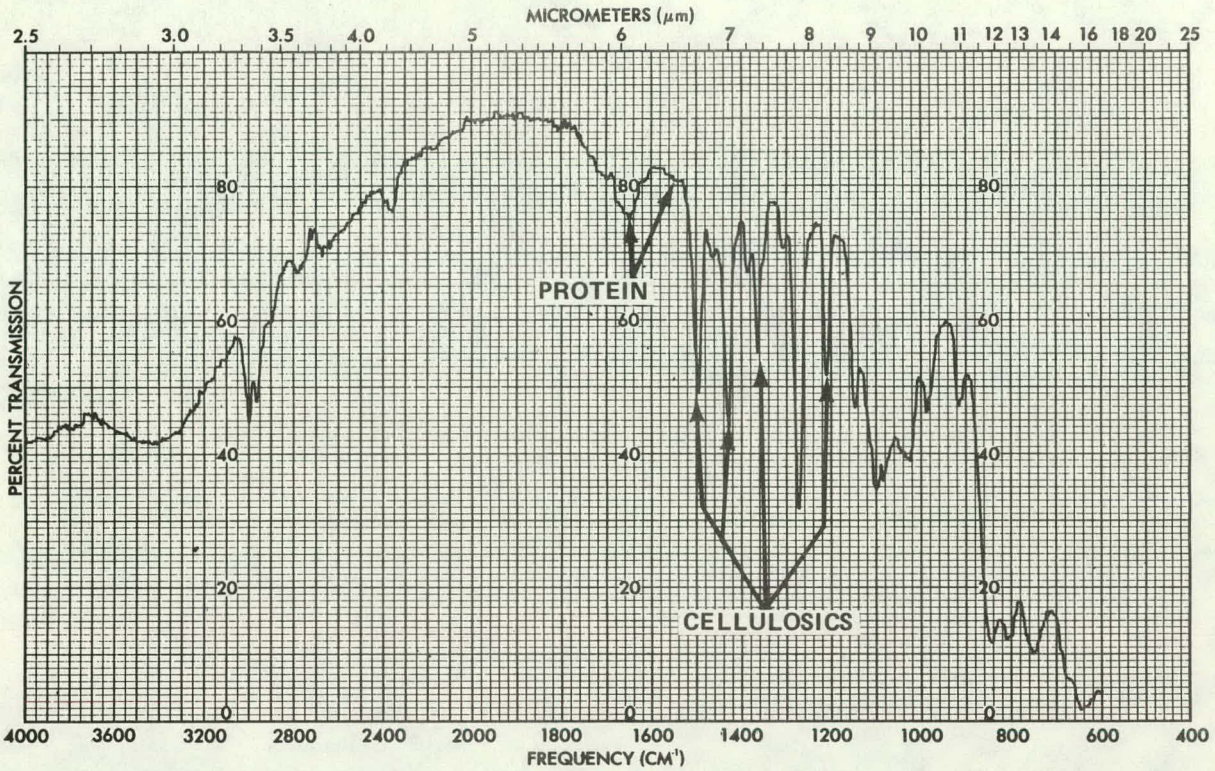
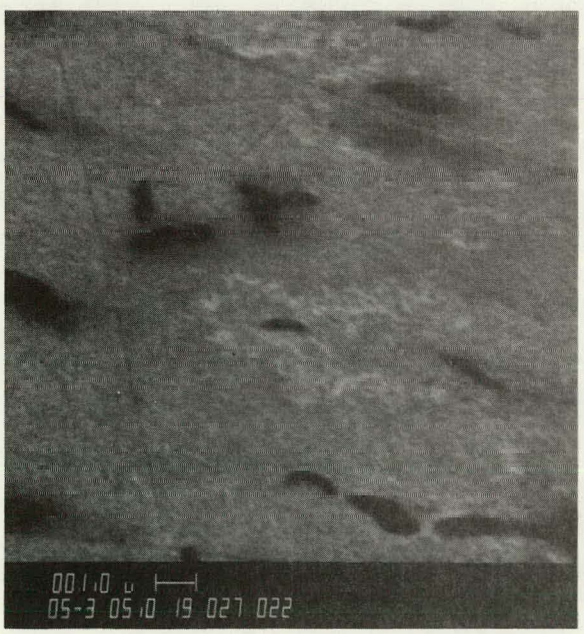
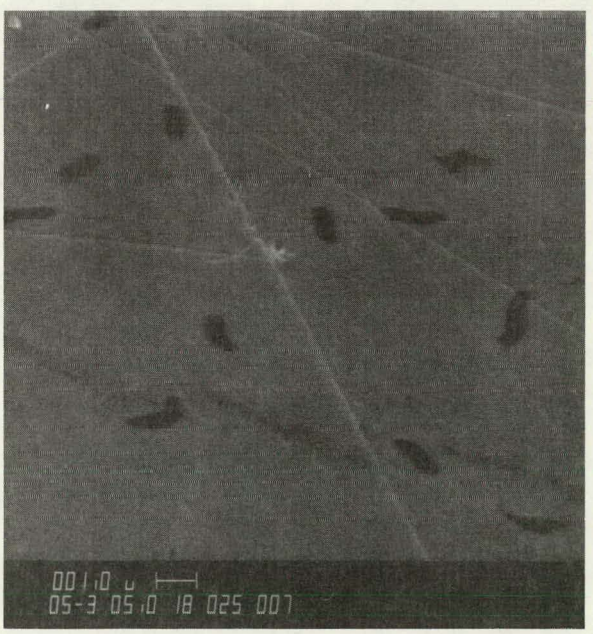


Figure 2 IR SPECTRUM OF PLATE COATED WITH DIMETHYLDICHLOROSILANE THAT WAS EXPOSED FOR 3 DAYS IN THE BARNACLE TANK SYSTEM

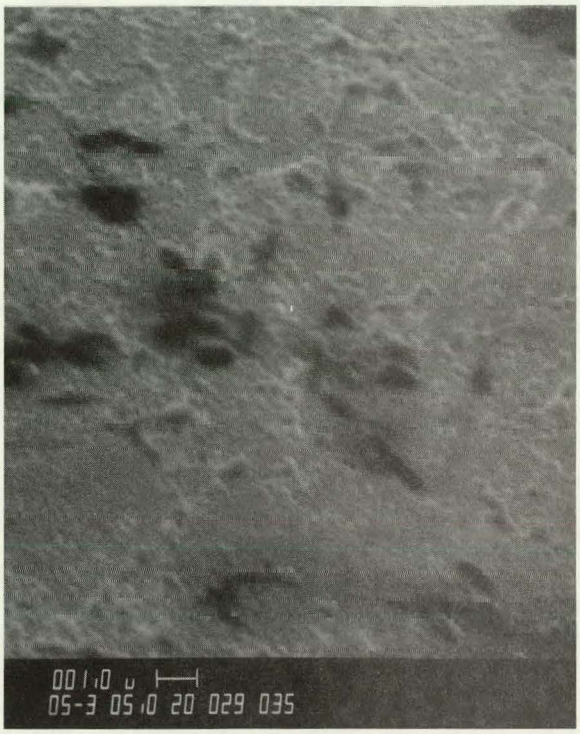


DETERGENT WASHED SUBSTRATE, 3 DAYS EXPOSURE

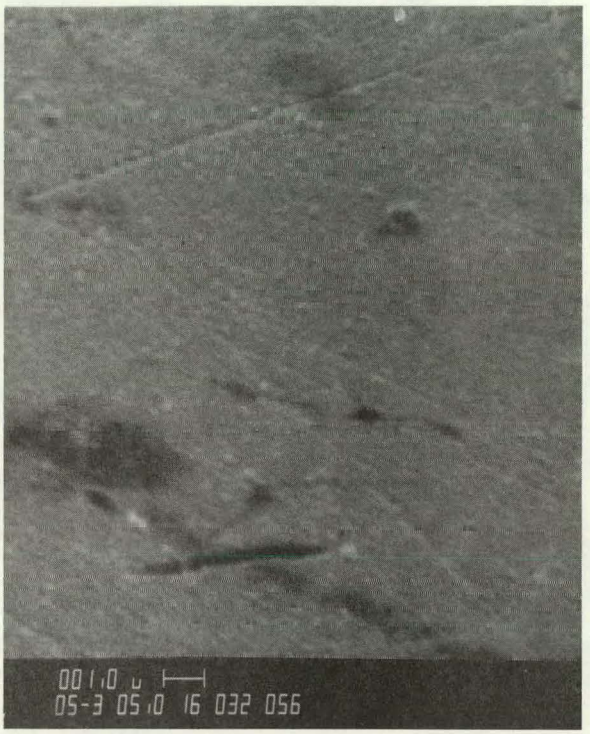


GLOW DISCHARGE TREATED SUBSTRATE, 1 DAY EXPOSURE

Figure 3 REPRESENTATIVE SEM PHOTOS (5000X) OF EXPOSED PLATES SHOWING PRESENCE OF BACTERIA



6 DAYS



12 DAYS

Figure 4 SEM PHOTOS (5000X) OF DIMETHYLDICHLOROSILANE-COATED PLATES THAT WERE EXPOSED TO SEAWATER FOR 6 AND 12 DAYS. NOTE THE SLOUGHING OF THE ADSORBED ORGANIC FILM AT 6 DAYS AND THE LESS FOULED SURFACE AT 12 DAYS.

with the exception of heptafluor surfaces, increased in thickness throughout the exposure period, indicating bioadhesive qualities. We will reserve any conclusions on the heptafluor until more data are acquired. The heptafluor's pre- and post-exposure γ_c's are very close to the nonbioadhesive range of 20-30 dynes/cm and may account for the film thicknesses observed.

Questions to be addressed upon completion of all of the exposure experiments include:

- Is there an ordering of bacteria on the surfaces through time? Do rod-shaped bacteria exclusively dwell on the surfaces before other types arrive?
- Does the Amide I-to-Amide II absorbance ratio change as a function of bacterial density?
- Does the heat exchange ability of the test plate change as a function of adsorbed film thickness in this microfouling range? As a function of adsorbed film chemistry?

Heat Exchange Experiments

Accelerated calibration experiments with the heat exchange flow cell system (Figure 5) have been done with fresh, raw milk at different temperatures. The high protein and mineral content milk experiments were carried out first primarily to evaluate our system with this quickly fouling media. Typical fouling in dairy heat exchange systems takes place in 6 to 24 hours.

The milk experiments, lasting several days each, were carried out using normal holding and pasteurizing temperatures of 40°F and 158°F and room temperatures of approximately 80°F (Figure 6). One observation from these tests was that the cold and room temperature heat exchange retardation was greater than in the high temperature test, substantiating the dairy industry's claim of the advantage of pre-heating before pasteurization.

Heat exchange flow cell work is underway in our seawater aquaria system. The first exposure test with the heat exchange flow cell is in Set III. The cell contains 2 germanium plates coated with dimethyldichlorosilane and will be exposed for 12 days. The heat cycling of the cell is done routinely by applying a 13-volt, 0.25 amp current to the externally insulated copper blocks for 1.5 minutes, resulting in a temperature increase of approximately 2°F.

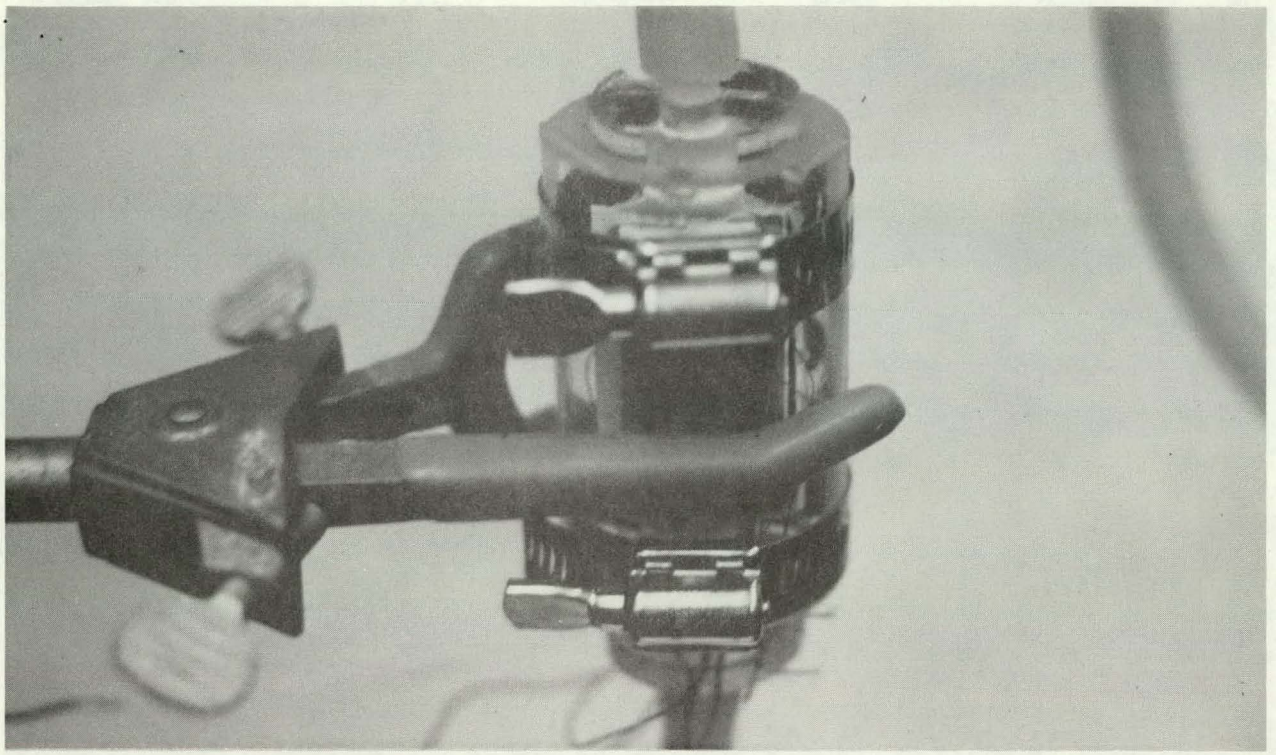


Figure 5 PHOTO OF HEAT EXCHANGE FLOW CELL. LIQUID FLOWS FROM BOTTOM TO TOP.

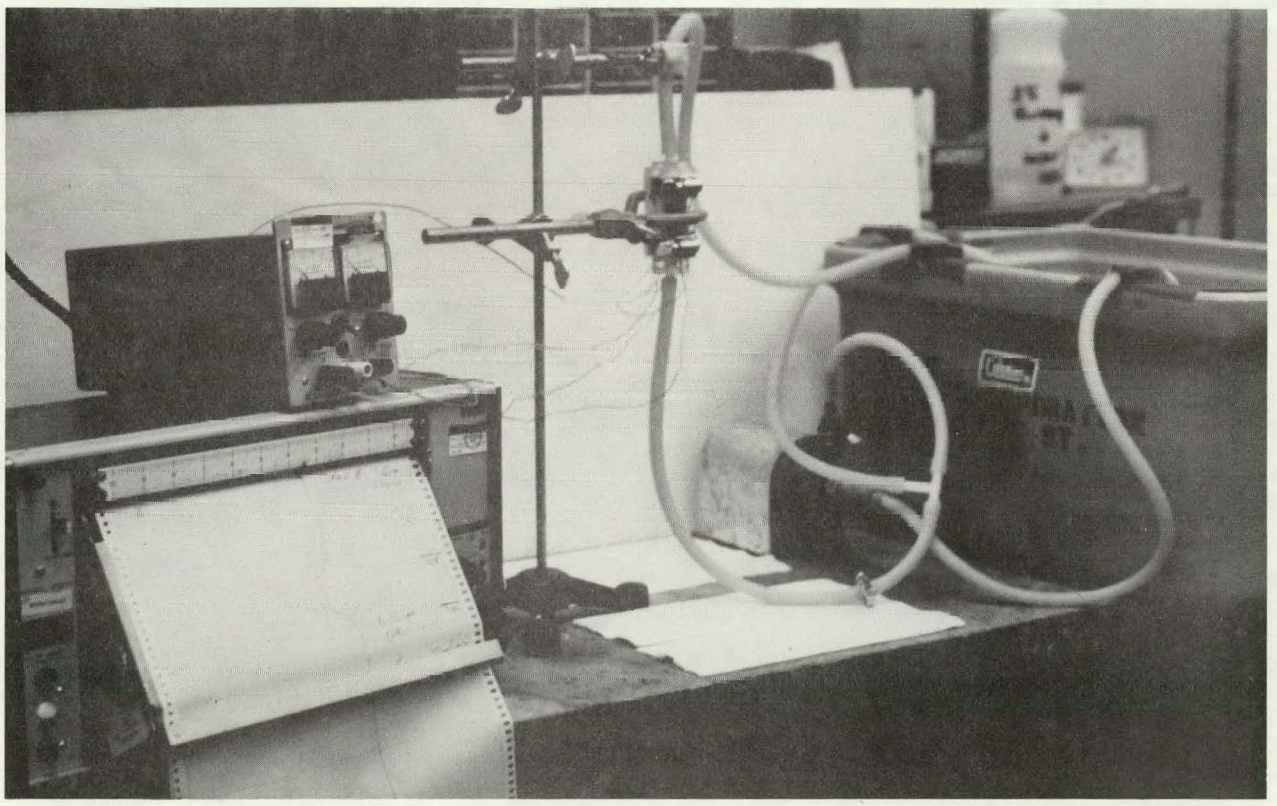


Figure 6 PHOTO OF ROOM TEMPERATURE MILK EXPERIMENT USING HEAT EXCHANGE FLOW CELL.

The heat-up and decay curve charts' read-outs (Figure 7) will be compared throughout the experiments for heat exchange retardation from fouling film build-up. Production of more heat exchange flow cells is in progress in order to carry out additional experiments in Sets IV and V. The electronics package for the system is in the final design stage at the present time.

Planned Project Activity - June to August 1981

- o Finish exposure experiments.
- o Prepare and submit annual report.

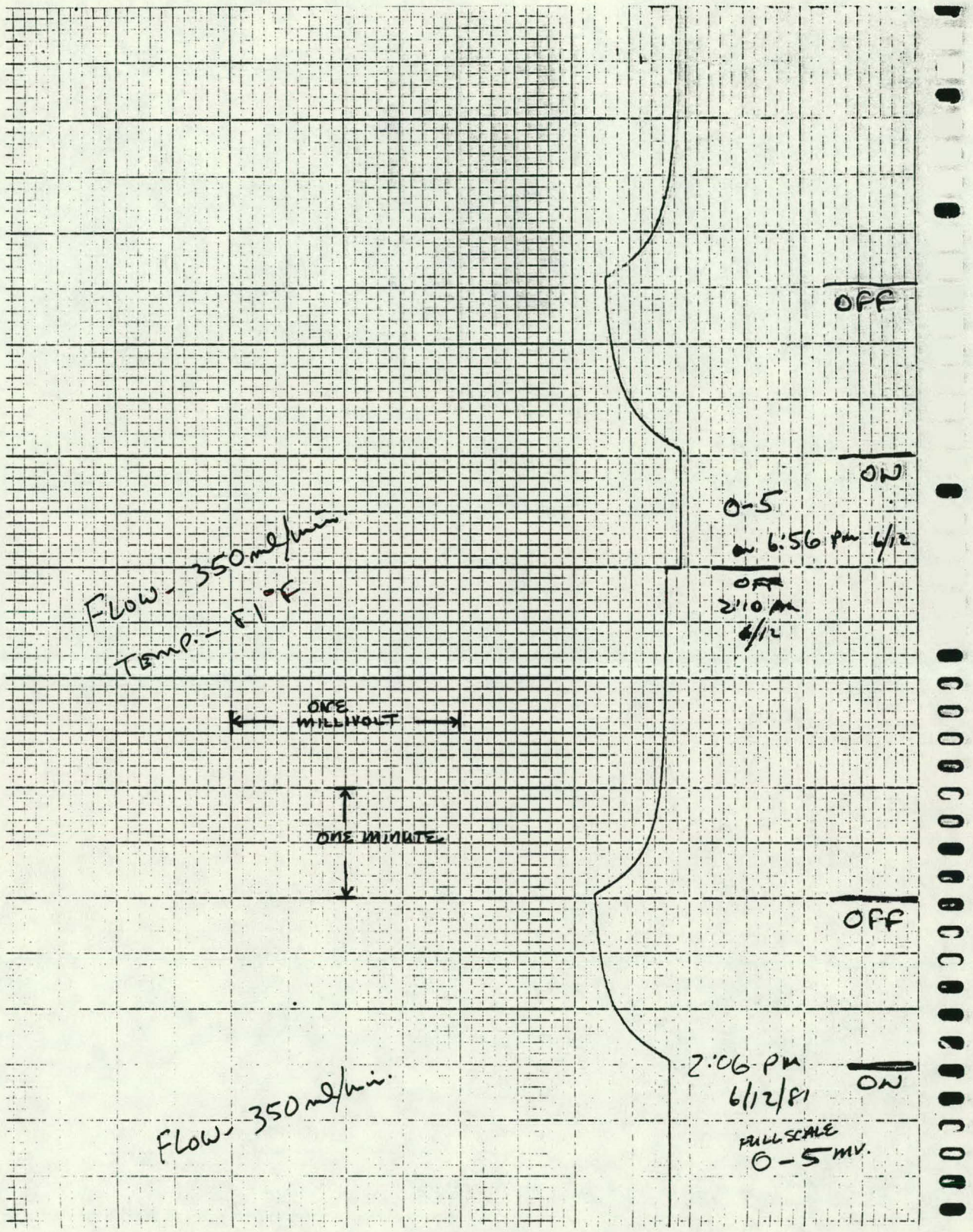


Figure 7 RAW DATA CHART FOR HEAT EXCHANGE FLOW CELL BEING EXPOSED TO SEAWATER (CHART SIZE REDUCED FOR THIS FIGURE)