Deposition and Corrosion Phenomena on Aluminum Surfaces Under Deluged Dry Cooling-Tower Conditions

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Prepared by
Battelle, Pacific Northwest Laboratories
Richland, Washington

U.S. DEPARTMENT OF ENERGY
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MASTER

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Prepared by
Battelle, Pacific Northwest Laboratories
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ABSTRACT

Deposition and corrosion on aluminum heat exchanger surfaces resulting from deluge in wet/dry cooling towers is simulated in a laboratory Corrosion/Deposition Loop (CDL). Heat exchanger deposition buildup was found to be linearly dependent on concentration factor and number of wet/dry cycles. Deionized water rinsing after deluge reduced rate of deposition.

Laboratory data obtained from CDL relates directly to operation of the Advanced Concepts Test (ACT) demonstration cooling tower. Technology transferable to ACT shows that deposition from supersaturated solution can be effectively controlled by attention to water chemistry, pH, water conditioning, and good heat transfer design. The additional mechanism of deposition by water film evaporation is effectively managed by soft water rinsing and uniform surface wetting.

Exposure of a model TRANE surface (the ACT wet/dry exchanger) produced short-term deposition extrapolating to 0.011 mm buildup in three years. Studies continue to verify 4X as maximum cycles of concentration through control of water chemistry and rinsing after deluge. Deluge water used at ACT facility is sufficiently aggressive to warrant use of Alclad to extend tube service life.

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EPRI PERSPECTIVE

PROJECT DESCRIPTION

A demonstration advanced wet/dry cooling system has been built at the Kern Station of Pacific Gas and Electric Company in Bakersfield, California. This system uses ammonia to transport the plant reject heat and utilizes advanced air-cooled heat exchangers and a steam condenser with heat transfer enhancements. The system offers the possibility of considerable savings in water, typically 75% compared to evaporative cooling systems, and total cost savings of nearly one-half compared to commercially available wet/dry cooling systems. When utilities find it necessary to use water-conserving cooling systems because of decreasing water availability, the ammonia system will offer the least expensive alternative identified to date, with a projected total savings to the industry of about $20 billion through the year 2000.

This project (RP422-3) is related to other EPRI research projects on the performance and economics of wet/dry cooling systems that are reported in:

- EPRI Final Report CS-1565, Test Report: Wet/Dry Cooling Tower Test Module, October 1980
- EPRI Final Report FP-1096, Optimization-Simulation Methodology for Wet/Dry Cooling, May 1979
- EPRI Final Report CS-1474, Wet/Dry Cooling for Cycling Steam-Electric Plants, August 1980
- EPRI Final Report CS-1594, User's Manual for WDCSIM II Wet/Dry Cooling Computer Program, October 1980

This interim materials report is the fifth in a continuing series that describes the Advanced Concepts Test (ACT) Facility Program. The others are:

- EPRI Summary Report CS-1324-SY, Power Plant Waste Heat Rejection Using Dry Cooling Towers, February 1980
- EPRI Interim Report CS-1530, Advanced Concepts Test Facility--Measurements and Suggested Test Plan, September 1980
- EPRI Interim Report CS-1668, Development of an Advanced Concept of Dry/Wet Cooling for Power Generating Plants, February 1981

- EPRI Interim Report CS-1915, Advanced Concepts Test (ACT) Facility Summary Safety Report, in press

PROJECT OBJECTIVES

The overall goal of the project is to develop and demonstrate a reliable and less expensive wet/dry cooling system to reduce cost impact as it becomes necessary to introduce more water-conserving systems and to improve power plant siting flexibility. The specific objective of this report is to summarize the results to date of a comprehensive, continuing corrosion and deposition study of the interaction of air, cooling water, and aluminum alloys under simulated wet/dry cooling-tower operating conditions.

PROJECT RESULTS

Results to date indicate that water deluge of extended air-cooled aluminum heat exchanger surfaces is a practical way to augment heat transfer in a wet/dry cooling tower. It should be possible to operate with a concentration of dissolved solids of a factor of about four (based on the makeup water at the Kern Station) without excessive deposition or concern for corrosion of the aluminum, provided that water chemistry is carefully controlled and that the surfaces are rinsed with deionized water before they are allowed to dry. This rinsing process does not have a major impact on system economics.

After the ACT acceptance test procedures are complete, plans call for a start of testing in August 1981 to demonstrate the technology for several years in a typical power plant environment. The feasibility of installing a materials evaluation test facility at the demonstration site is being considered.

Utility planners with concerns about increasing water scarcity for power plant cooling, the high costs of conventional wet/dry cooling, and constraints on plant siting should be interested in the conclusions regarding water deluge as an cooling augmentation technique. Results of deposition and corrosion on aluminum exposed to air and water should be of general interest.

John A. Bartz, Project Manager
Coal Combustion Systems Division

FOREWORD

The Dry Cooling Enhancement Program at the Pacific Northwest Laboratory (PNL) was initiated with a program scope that included the following near-term and ultimate emphases.

NEAR-TERM OBJECTIVES

- Develop economic and performance models for cost optimization of total heat rejection systems using dry cooling.
- Analyses of, and dissemination of experience on, existing dry-cooled plant performance.
- Demonstration of existing technology in dry cooling to strengthen basis for equipment specification by utilities.

ULTIMATE OBJECTIVE

- Provide economical cooling systems that conserve water for industry use by developing and demonstrating the reliability of such lower-cost systems. The development of advanced dry and wet/dry systems is considered to be within this scope.

The following documents have been issued, reporting the results of the work toward these objectives:

Cost Optimization of Dry-Cooled Heat Rejection Systems

A Review and Assessment of Engineering Economic Studies of Dry-Cooled Electrical Generating Plants. B. C. Fryer, BNWL-1076, March 1976.
Heat Transfer and Pressure Drop Characteristics of Dry Tower Extended Surfaces. Part I: Heat Transfer and Pressure Drop Data. PFR Engineering Systems, Inc., PFR 7-102, June 1976.

Analysis of Performance of Existing Dry-Cooled Plants

Dry Cooling Tower Program: Results of Industrial Contacts Through August 1974. F. R. Zaloudek and B. M. Johnson, BNWL-1878, November 1, 1974.

A Survey of Materials and Corrosion Performance in Dry Cooling Applications. A. B. Johnsdon, Jr., D. R. Pratt, and G. E. Zima, BNWL-1958, March 1976.

European Dry Cooling Tower Operating Experience. J. G. DeSteese and K. Simhan, BNWL-1995, March 1976.

Mathematical and Experimental Investigations on Dispersion and Recirculation of Plumes from Dry Cooling Towers at Wyodak Power Plant in Wyoming. Y. Onishi and D. S. Trent, BNWL-1982, February 1976.

Aluminum Alloy Performance Under Dry Cooling Tower Conditions, A. B. Johnson, Jr., S. Begej, M. W. Martini, and R. P. May, PNL-2292, December 1977.

Advanced Dry (Wet/Dry) Cooled Systems

Preliminary Evaluation of Wet/Dry Cooling Concepts for Power Plants. W. V. Loscutoff, BNWL-1969, July 1976.

Compatibility of Ammonia with Candidate Dry Cooling System Materials. D. R. Pratt, BNWL-1992, April 1976.

Scale Formation in Deluged Dry Cooling System. D. R. Pratt, BNWL-2060, March 1976.

Ammonia as an Intermediate Heat Exchange Fluid for Dry Cooled Towers. R. T. Allemann, B. M. Johnson, Jr., and G. C. Smith, BNWL-SA-5997, September 1976.

Conceptual Design Study, Advanced Concept Test (ACT) Facility. F. R. Zaloudek, PNL-2715, September 1978.

Augmented Dry Cooling Surface Test Program: Analysis and Experimental Results. H. L. Parry, L. J. MacGowan, D. K. Kreid, L. E. Wiles, D. W. Faletti, and B. M. Johnson, PNL-2746, September 1979.

An Engineering and Cost Analysis of a Dry Cooling System Augmented with a Thermal Storage Pond. M. K. Drost and R. T. Allemann, PNL-2745, September 1978.

A group of reports issued by this program serve the dual purpose of developing cost optimization models for dry cooling systems based on available technology and comparing the results of analyzing the costs of these systems with the projected cost of several advanced dry and wet/dry systems. Included in this group are:

An Engineering and Cost Comparison of Three Different All-Dry Cooling Systems. B. C. Fryer, D. W. Faletti, Dan J. Braun, David J. Braun, and L. E. Wiles, BNWL-2121, September 1976.

A Study of the Comparative Costs of Five Wet/Dry Cooling Tower Concepts. F. R. Zaloudek, R. T. Allemann, D. W. Faletti, B. M. Johnson, H. L. Parry, G. C. Smith, R. D. Tokarz, and R. A. Walter, BNWL-2122, September 1976.

Dry Cooling of Power Generating Stations: A Summary of the Economic Evaluation of Several Advanced Concepts Via a Design Optimization Study and a Conceptual Design and Cost Estimate. B. M. Johnson, R. T. Allemann, D. W. Faletti, B. C. Fryer, and F. R. Zaloudek, BNWL-2120, September 1976.

Costs and Cost Algorithms for Dry Cooling Tower Systems. P. A. Ard, C. H. Henager, D. R. Pratt, and L. E. Wiles, BNWL-2123, September 1976.

A User's Manual for the BNW-I Optimization Code for Dry-Cooled Power Plants. David J. Braun, Dan J. Braun, Warren V. Demier, D. W. Faletti, and L. E. Wiles, BNWL-2180, January 1977.

Comparative Cost Study of Four Wet/Dry Cooling Concepts That Use Ammonia as the Intermediate Heat Exchange Fluid. R. D. Tokarz, Daniel J. Braun, B. M. Johnson, R. T. Allemann, David J. Braun, H. L. Parry, G. C. Smith and F. R. Zaloudek, PNL 2661, May 1978.

A Description and Cost Analysis of a Deluge Dry/Wet Cooling System. L. E. Wiles, J. A. Bamberger, Daniel J. Braun, David J. Braun, D. W. Faletti, and C. E. Willingham, PNL-2498, June 1978.

A User's Manual for the BNW-II Optimization Code for Dry/Wet-Cooled Power Plants. Daniel J. Braun, Judith A. Bamberger, David J. Braun, Duane W. Faletti and Larry E. Wiles, PNL-2674, May 1978.

Three reports have been issued which consider the future need for any cooling and the potential benefit/cost ratio of a large-scale demonstration.

An Overview of Economic, Legal, and Water Availability Factors Affecting the Demand for Dry and Wet/Dry Cooling of Thermal Power Plants. P. L. Hendrickson, BNWL-2268, Rev. September 1978.

Estimation of Benefits from Demonstrating Advanced Dry Cooling Technology: A Framework and Partial Analysis. J. W. Currie and T. J. Foley, BNWL-2182, April 1977.

Potential Use of Dry Cooling in Support of Advanced Energy Generation Systems. D. W. Mayer, E. M. Arnold, and R. T. Allemann, PNL-3149, March 1980.

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This work was conducted under the Dry-Cooling Enhancement Program at Pacific Northwest Laboratory (operated by Battelle) and was sponsored jointly by the Department of Energy, Division of Advance Systems and Materials Production, under Contract EY-76-C-06-1830 and the Electric Power Research Institute under Project RP422-3.

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SUMMARY AND CONCLUSIONS

Battelle's Pacific Northwest Laboratory (PNL) is manager for a program jointly funded by the Department of Energy (DOE) and the Electric Power Research Institute (EPRI) to develop advanced Dry and Water Augmented Dry Cooling for electric power generation. In support of this dry cooling enhancement program, a Corrosion/Deposition Loop (CDL) is being operated at PNL to study the interaction of cooling water and aluminum alloys under simulated wet/dry tower conditions.

An aluminum heat transfer surface of HOTERV design and an aluminum plate are exposed to recirculating cooling water with controlled composition and pH. Evaporative losses from the open system are replaced by automatic addition of deionized (DI) water. Internal heating provides a 50 to 54°C surface temperature at the water-metal interface.

Deposition of dissolved solids on heated surfaces occurs primarily from two causes: 1) decreasing solubility of certain salts with increasing temperature, and 2) deposition of dissolved solids as water films evaporate. Corrosion/deposition was evaluated as a function of untreated water composition, pH, water and metal surface temperatures, and water additives. The CDL was operated in both cyclic (with film drying) and steady-state (continuously wet) modes.

The first seven exposures of the HOTERV core were done in the Mod-1 design in cyclic (30 min wet, 15 min dry) operating mode. The cooling system contained approximately ten liters of simulated Kern well water for deluge. Core heat flux was supplied by resistance heaters inserted in selected core tubes.

Weight gain caused by deposition in this low water volume system was observed to be linearly dependent on both concentration factor of the simulated site water and the number of wet/dry cycles that the specimen surfaces experienced. Rinsing with deionized water after deluge reduced the rate of weight gain, although the linear relationship was maintained.

Most of the deposition occurred on and near the hot tubes containing electric heaters. Thus, although the Langelier and Ryznar indices of the cooling water suggested minimum steady-state scaling at the 49^{o}C indicated core temperature, substantial steady-state scale was accumulating on hot tubes. Deposition by the evaporation mechanism also contributes to overall weight gain, an observation supported by the reduction in weight gain rate seen when a short rinse substantially removes the deluge film after each 30 min wet cycle.

Several operating characteristics of the CDL during early runs were not representative of industrial towers. Low inventory of scale forming ions, low deluge flow rate and local hot spots contribute to a scaling pattern which is difficult to project to a large cooling tower. To overcome these uncertainties, the CDL was re-designed (Mod-2) to give a 10X increase in available deluge volume, a greater deluge flow rate with improved water dispersion, and a heating system to eliminate core tube temperatures above 55^{o}C.

The immediate consequence of increasing the supply of low solubility ions was an increase in deposition when compared to a prior run with equivalent water chemistry and exposure time. Lowering the pH to a neutral 7.0-7.5, however, reduces the bicarbonate ion concentration and the formation of $CaCO_3$, the chief scaling compound in these waters at these temperatures.

Other modifications in system design or procedure introduced after Run #7 were: increased deluge flow rate, improved water distribution, increased length of rinse cycle, and addition of a low (2 ppm) concentration of a commonly used polyphosphate water softening agent. The net effect of all these modifications was to bring the core weight gain at 4X concentration water within acceptable limits for scale buildup over a projected 30 yr cooling tower service life. The use of chemical additives to cooling water for scale control and/or cleaning needs additional in-depth evaluation.

The first exposure of the model TRANE core at 2X water concentration produced a weight gain of only 7.5 mg/dm^2 after 130 hr of cyclic exposure. This projects to an estimated 0.011 mm uniform scale thickness in three yr. The buildup, however, is not uniform but is concentrated in certain areas. Deposition on the corrugated fins was confined primarily to ridges, suggesting possible low deluge flow in these locations. Substantial deposition may occur by an evaporative mechanism during deluge due to splashing or regions of low flow (ridges). This non-uniform buildup can affect air pressure drop significantly before it influences thermal resistance.

Based on CDL data to date, deluge is a viable method for dry cooling enhancement. Several more CDL exposures of the TRANE surface are needed to define Advanced Concepts Test (ACT) deluge operating procedures. Uncertainty still exists in recommending 4X concentration as an upper operating limit since the mechanisms for deposition on the TRANE core are not clearly understood. Several TRANE surface exposures in actual Kern water gradu- ally concentrating to 4X will provide the basis for recommendation. The role of rinsing in regulating evaporative deposition will be more closely defined.

Kern well water is sufficiently aggressive on aluminum alloys to warrant a form of protection against pitting corrosion under surface deposits or in crevices at the tube-fin junction. The TRANE heat exchangers for the ACT facility will employ Alclad 3003 alloy, furnishing cathodic protection against galvanic attack. Samples of these alloys are now undergoing evaluation of their resistance to attack by Kern well water.

The feasibility of establishing a materials corrosion evaluation test loop at ACT is being studied.

Section 1

INTRODUCTION

The large-scale use of water for cooling purposes by central power stations is becoming increasingly problematic because of environmental restrictions, increasing demand for water for other uses and increasing water costs. These factors may make dry cooling necessary before the end of this century in some areas of the United States (1, 2). However, dry-cooled installations require a large initial capital investment and lose efficiency when the ambient air temperature is high. A proposed wet/dry system is being investigated to reduce water consumption, compared to a conventional wet tower, while avoiding high turbine backpressures on hot days. The system operates with dry-cooled modules until ambient air reaches a critical temperature. Operation is then switched to deluged modules. This reduces the capital investment, compared to a completely dry-cooled system, without as large an accompanying hot weather performance penalty.

1.1 PROGRAM OBJECTIVES

The Dry Cooling Enhancement (DCE) program at Battelle's Pacific Northwest Laboratory, jointly funded by the Department of Energy and the Electric Power Research Institute, has the objective of evaluating economical cooling systems that conserve water for the electric power generating industry. Corrosion was identified in an initial survey (3) as a potentially costly factor that should be assessed in dry-cooled installations to minimize operating costs of future plants.

Previous reports (4, 6) have summarized materials performance in a cross section of the U.S. and foreign dry-cooled installations and have indicated that dry-cooled equipment generally functions with a minimum of operational problems, with a few exceptions where environments are particularly aggressive. However, the deluging concept for dry-cooled installations imposes the potential for deposition (scaling) and an expanded potential for corrosion beyond that encountered in the all-dry-cooled unit. Operators of some small industrial dry-cooled units have sprayed highly impure water on the finned surfaces on hot days, eventually resulting in loss of efficiency due to a combination of deposition and corrosion (5).

This study contributes to the overall DCE program by providing corrosion/deposition data which will have a direct application to the water quality standards selected for the deluge water used on the DCE Advanced Concepts Test (ACT) dry-cooling tower. This interim report presents results to date of corrosion and deposition on aluminum surfaces obtained in a laboratory loop under conditions simulating deluged dry-cooled operation. The emphasis in work reported here is on deposition rather than corrosion.

1.2 EXPERIMENTAL OBJECTIVES

The corrosion/deposition loop (CDL) is an experimental facility designed to evaluate the effects of water composition on scaling tendency and deposition mode on exterior surfaces of fins under simulated deluged dry-cooling tower conditions. The primary objective of the initial experiments was to simulate the deposition on a deluged aluminum air-cooled heat exchanger operating with the known cooling water impurity composition at the site of the ACT facility. From this information, estimates of water treatment needed to assure a reasonable lifetime for deluged dry-cooled units can be made based on water quality at that site. The site chosen was the Kern County power plant of Pacific Gas and Electric Company at Bakersfield, California. The CDL tests were intended to help determine modes of deposition and factors affecting rate of deposition.

An experimental objective of secondary importance was to determine if the Langelier and Ryznar indexes (7, 8) would predict scaling on heated surfaces that are subjected to repeated cycles of wetting and drying. These two indexes are valuable for determining the approximate limits on impurity levels but the scaling predictions apply only to saturation type scaling during steady-state water flow. It is suspected that residual deposition due to cyclic wet/dry operation cannot be predicted by either the Langelier or the Ryznar indexes. Since these indexes do not appear to apply directly to scaling predictions for periodically deluged surfaces, sufficient corrosion and deposition data must be obtained to predict scaling empirically as a function of water chemistry, water temperature, surface temperature and the number of deluge cycles.

The deposition that occurs during these experiments is expected to be primarily a function of the total dissolved solids (TDS) in the water film left on the surface during incomplete wetting or at the end of each deluge cycle. The saturation type scaling mode theoretically will be largely suppressed by controlling the water chemistry in the range which the indices predict to be non-scaling. Nomographs are available in several forms for computing these indices (9, 11).

1.3 SCOPE OF EXPERIMENT

The well water at the ACT site was analyzed and the constituents at the desired concentration factor were determined. A HOTERV core together with plate-type specimens, both anodized and unanodized, were deluged and dried for a measured number of cycles during each test. The delugate compositions represented concentration factors of 2 to 5 times the natural source water composition of the ACT site.

1.3.1 CDL Mod-1 (Cyclic)

A total of eight test runs were completed and evaluated for deposition and/or corrosion. Distribution, formation mode, composition and other characteristics were evaluated for both deposition and corrosion on the specimens. The effects of rinsing specimens with deionized water (DIW) after the deluge flow had ceased were evaluated for deposition changes.

1.3.2 CDL Mod-2 (Steady-State)

Nine additional runs were conducted in the CDL to scope the contribution of steady-state deposition to total scaling. The effect of impurity concentration, pH, and water conditioning were emphasized. The CDL was modified to give a greater solute species inventory, a uniform core heat, and longer rinse cycles.

1.3.3 Anodizing

The effect of anodizing was examined for changes in corrosion of plate specimen surfaces. Anodizing was carried out in an oxalic acid bath at 19°C, 16 milliamps cm^{-2} and 50 to 70 volts for 45 minutes. The coat was sealed in boiling deionized water.

Section 2

EXPERIMENTAL SYSTEM

The corrosion/deposition loop (CDL) is designed to perform studies of deposition on heated aluminum surfaces normally cooled by a flowing air stream but subject to periodic deluging with impure water. Corrosion is being studied also, but because it cannot be accelerated as the deposition studies can be, corrosion evaluations had a secondary role in the results reported here.

2.1 CDL MOD-1 DESCRIPTION

The CDL was designed to simulate the air flow, element temperature, cyclic water flow, and heat transfer conditions typical of a deluged dry cooling tower (DCT). The loop can simulate many wet/dry cycles in a short time. This small-scale facility has components which heat and deluge specimens under controlled induced air flow and temperature. The temperature is measured and recorded at several points. Specimen accessibility for observation and easy removal is a feature of the loop. Figure 2-1 is a perspective drawing of the CDL; Figures 2-2 and 2-3 are a front and top view of the CDL, respectively.

The CDL facility has three main operating sections: 1) an air duct to provide a controllable air flow through the DCT elements, 2) a deluge water system to periodically deluge the specimens with water at a controlled temperature and flow rate, and 3) a monitoring/control system that provides for a correct specimen temperature (via electric heaters for Mod-1) and recording of temperature at numerous points in and on the specimens, the air flow and the water system.

The air duct is an open-ended single-pass system that encloses the test specimens and provides a catch basin for the deluge water. Laboratory air enters the duct at ambient temperature, passes through the test specimens, and is exhausted back into the laboratory. Pressure plates (20% open) are positioned before and after the duct section that contains the specimens to smooth the air flow. The downstream air duct section has 10 holes (~8 cm dia) in the top cover to allow air to bypass the test section to assist in controlling air velocity. Additionally, a damper at the entrance of the air duct controls air flow through the specimens to the desired velocity as measured by an air velocity meter. Test operating

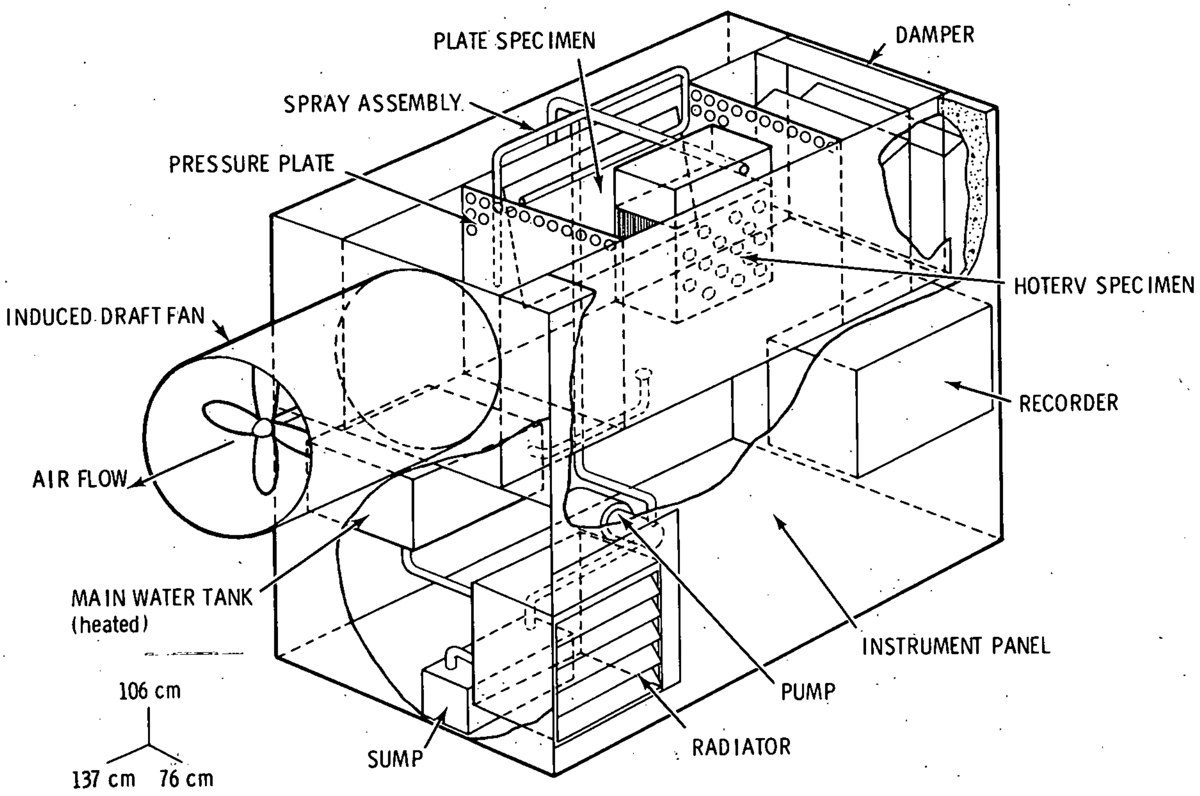

Figure 2-1. Corrosion/Deposition Loop CDL Mod-1

velocity was 1 m/sec through the specimens. A plexiglas air baffle in the test section blocks all air flow that would bypass the specimens.

The deluge water system (Figure 2-4) consists of a spray bar and spray dispersion screen designed to form a thin uniform water film over the test elements.

Water containment components are stainless steel. The system has a radiator fan and tank immersion heater that are temperature controlled, so that the deluge water temperature can be maintained nearly constant. The heater and fan cannot be run simultaneously. The pump is controlled by a timer capable of switching 32 cycles/day (30 min on, 15 min off). Evaporative losses are automatically made up as evaporation occurs by piping deionized water directly to the immersion heater tank when the samples are not to be rinsed. To rinse the specimens with deionized water immediately after the deluge cycle, the evaporative loss is <u>only</u> made up immediately after the deluge water shuts off by introducing this deionized water as a specimen rinse via a series of automatic valves. Thus, no automatic makeup water is provided during the deluge cycle itself.

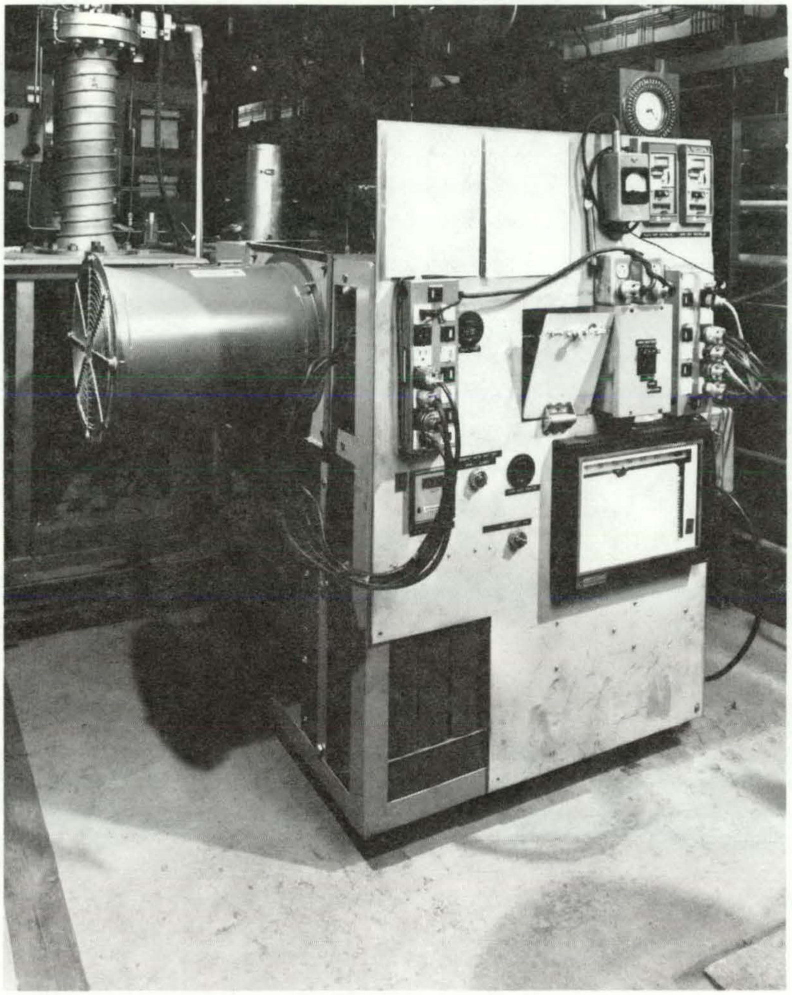

Figure 2-2. Front View of CDL Mod-1

The monitoring/control system maintains, controls, and records the temperature of the test specimens and the water system and records the air temperature as well. Temperatures from a total of 15 points were measured and recorded by this system.

Temperature measurements were taken as follows:

Location	Number of Measuring Points
Plate	4
HOTERV core	7
Inlet air flow	1
Exit air flow	1
Water flow	2

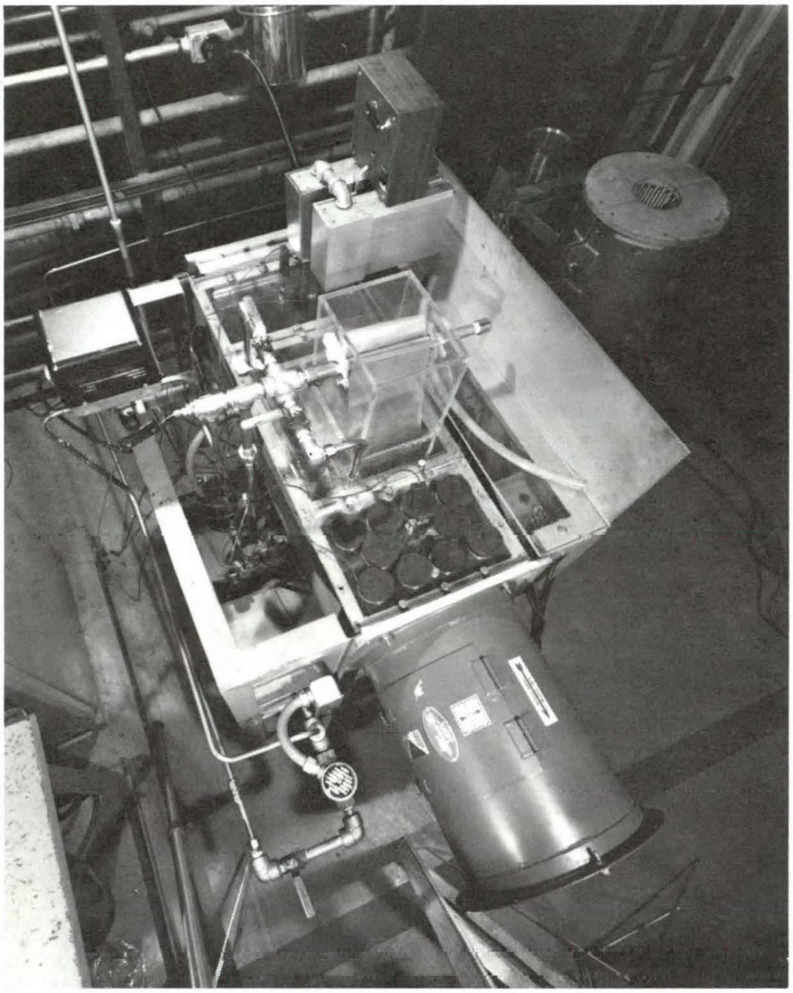

Figure 2-3. Top View of CDL Mod-1

2.1.1 CDL Mod-2

The cartridge heater method in CDL did not satisfactorily simulate core heating in large-scale towers. A closed water loop was substituted for electrical tube heaters. Hot, deionized water from a regulated temperature reservoir now circulates through all core tubes, supplied from common entrance and exit manifolds. The single pass system produces a uniform, preselected temperature over the entire core. Water circulates at approximately 37 liter/min at a nominal 52^{O}C temperature to approximate the ACT ammonia loop. Thermocouples monitoring the entrance and exit water temperatures show no measurable temperature drop across the 15-cm long HOTERV core.

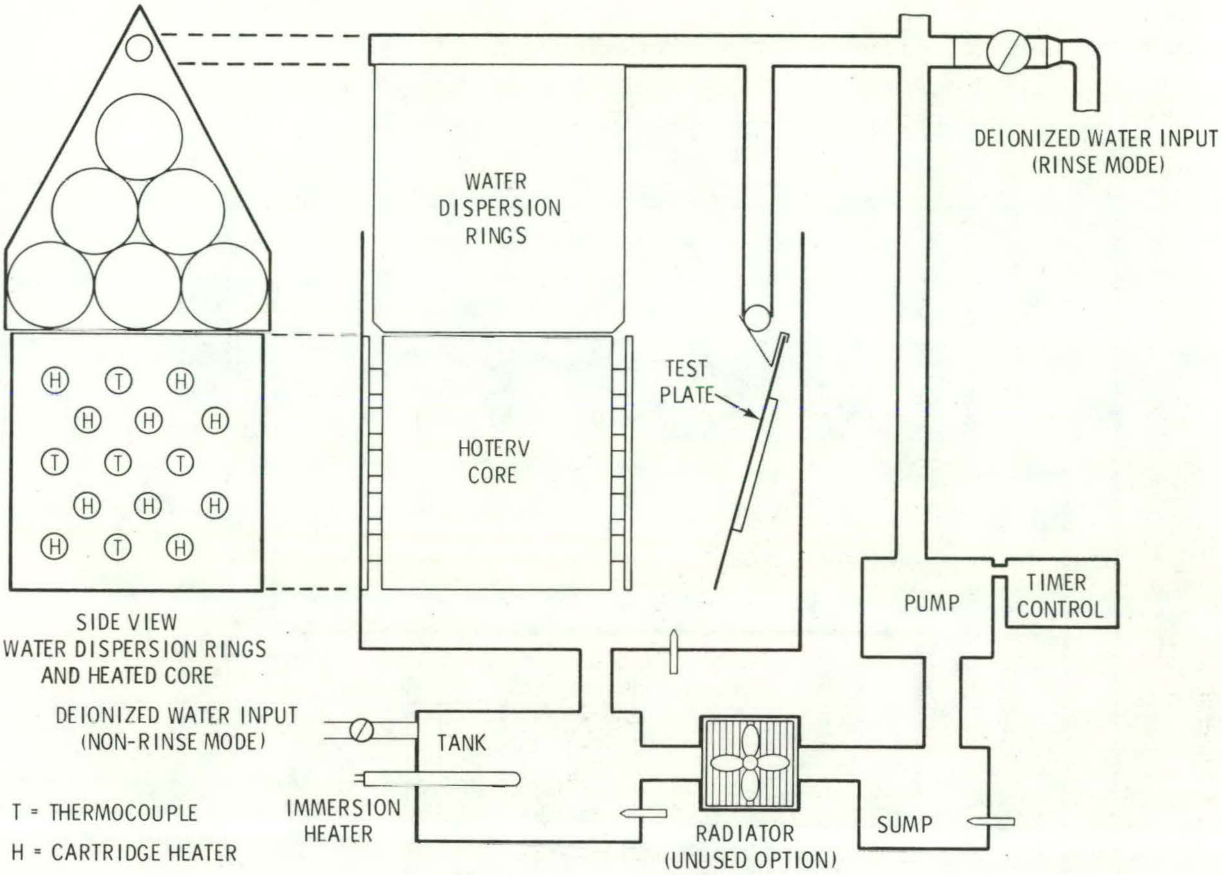

Figure 2-4. Block Diagram of Water System for CDL Mod-1

Additional minor CDL modifications included an enlarged deluge piping system to permit wider variation of deluge flow rate, and installation of a variable time to the rinse circuit. The water distribution mechanism for deluging was altered to wet the entire core uniformly at a flow rate of 7.5 liter per min over the 15-cm length which is high in comparison to the 2.8 liter per min/15 cm for ACT design. A flat test plate for materials corrosion evaluation was unaltered from prior runs. It was heated by a flat resistance element and wetted by the core deluge system. A schematic of the modified CDL is seen in Figure 2-5. The actual physical assembly is seen in Figure 2-6a,b.

2.2 DESCRIPTION OF EXPERIMENT

2.2.1 CDL Mod-1

Eight test runs were conducted. Five test runs were eight days in length; the other three test runs were 2, 16 and 24 days long. Deluge cycle length was

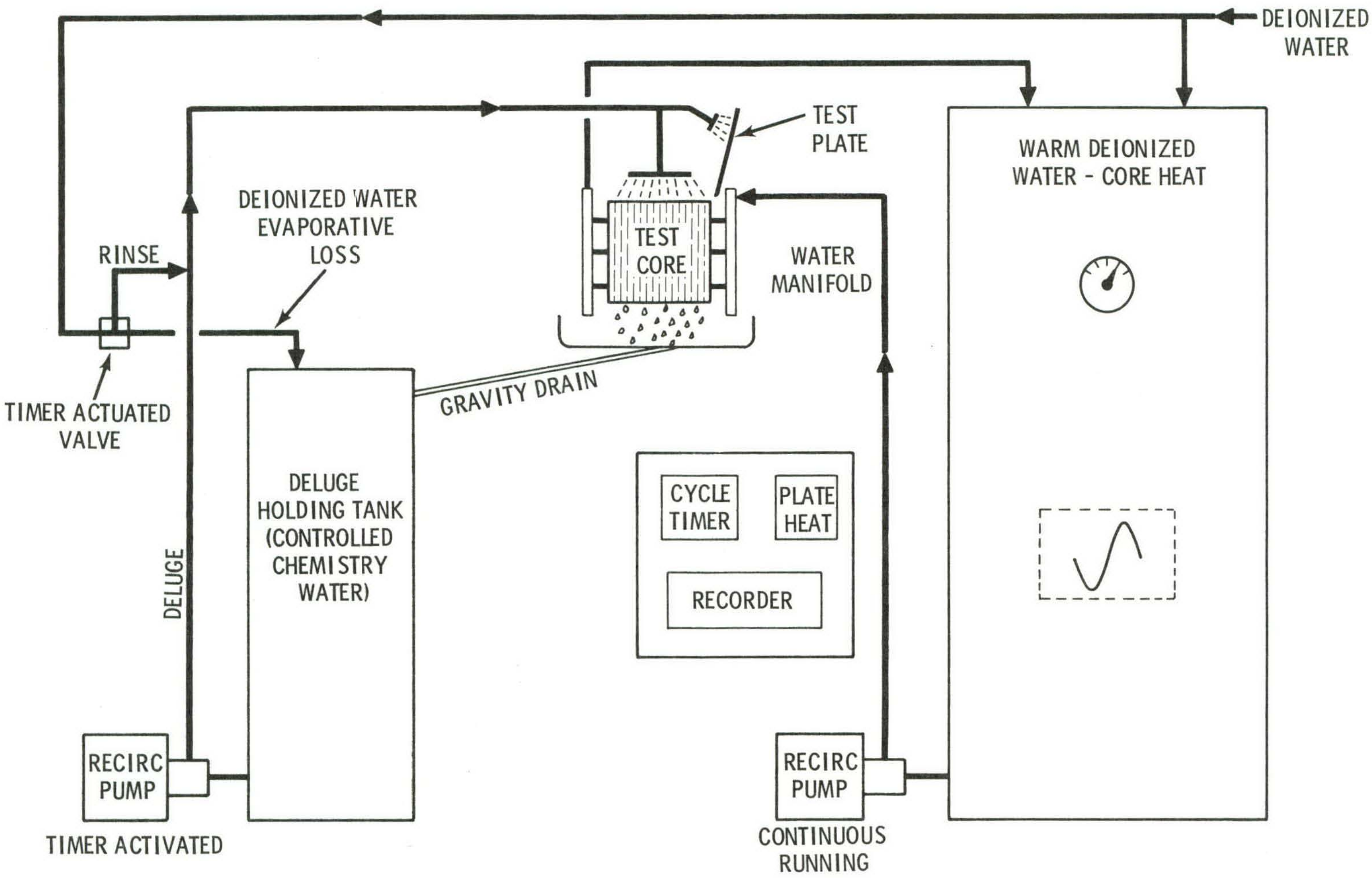

Figure 2-5. Block Diagram of CDL Mod-2

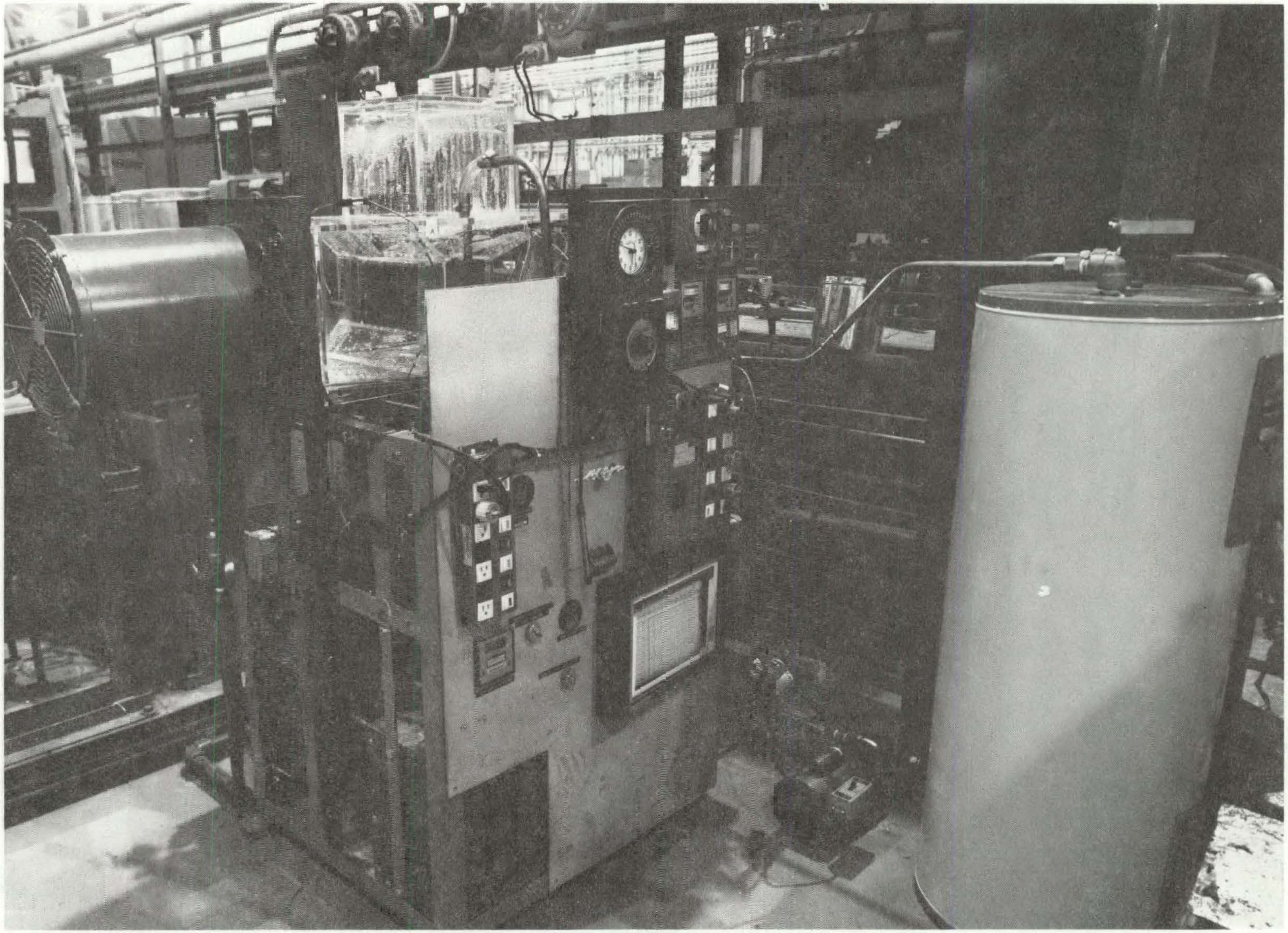

Figure 2-6a. Front View of CD_ Mod-2

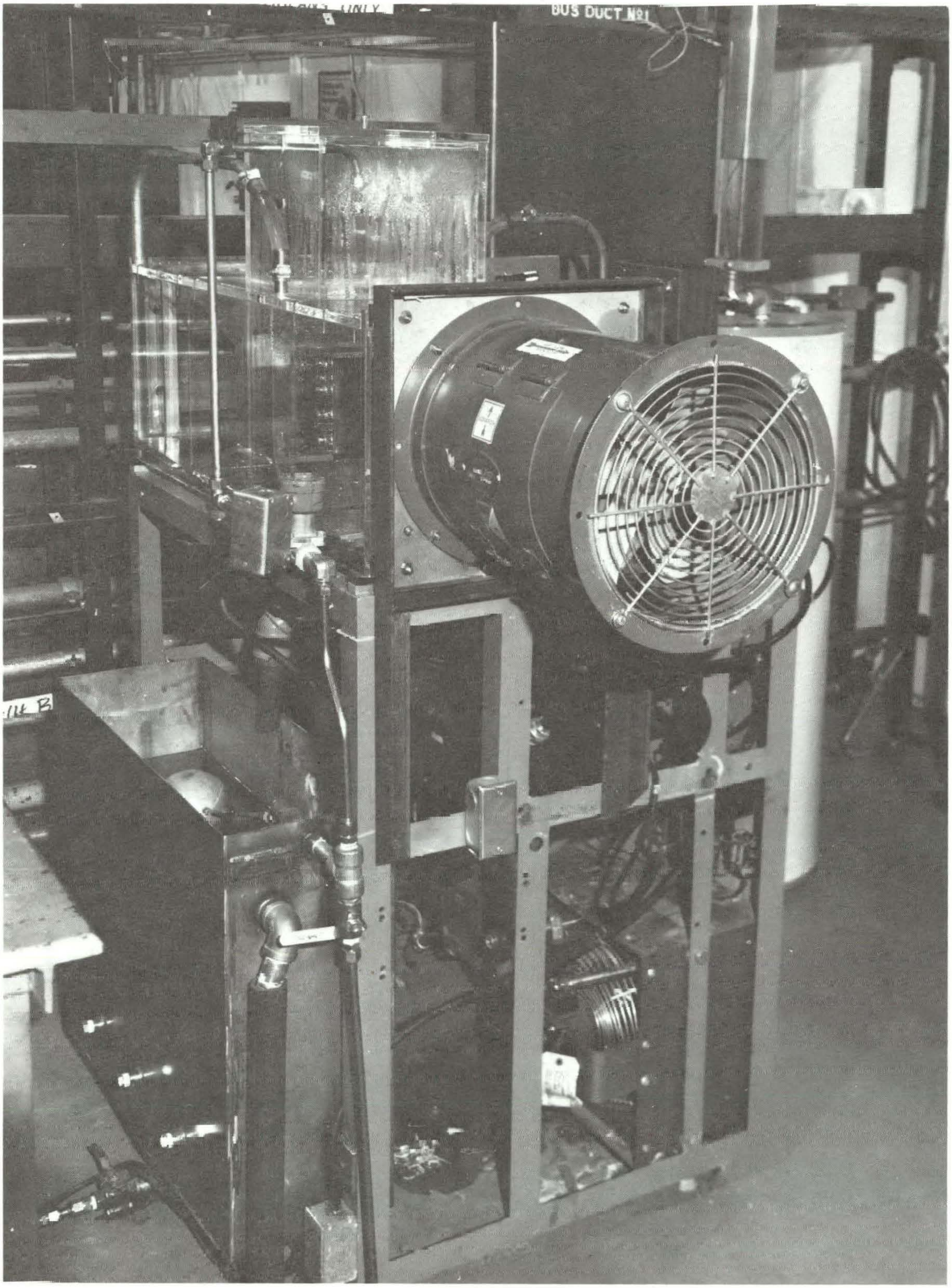

Figure 2-6b. Side View of CDL Mod-2

45 min: 30 min deluged and 15 min dry. This allows 32 cycles/day. The maximum concentration factor for the original ACT site well water is approximately 5X due to its high SiO_2 content. The CDL tests were done with water concentration factors of 2X, 3X and 4X.

The first six test runs were with deluge but not with a rinse with "clean" water before drying. During the last two test runs, the specimens were rinsed with deionized water (DIW) prior to drying.

A daily water analysis determined pH, conductivity and concentration of selected ionic species in the delugate. Water and core temperatures were continuously recorded.

Weight measurements, optical metallography, scanning electron microscopy (SEM) and SEM microprobe analysis are the principal means by which the specimens were examined and changes determined.

2.2.2 CDL Mod-2

Nine test runs were conducted by operating the CDL in continuous deluge with one drying at the end of the normally 125-hr long wet exposure. Water concentrations were varied between 2X and 5X with deionized water added to compensate for evaporative loss.

A slow drip of the appropriate concentration was added to nearly all runs to stabilize concentration of the initial value throughout the run. Water pH was continuously monitored and acid was added to maintain the selected pH level.

Runs #16 and #17 were cycled with a two-min deionized water rinse after each wet cycle.

Water analysis was done daily as in Mod-1. Weight measurements, visual interpretation, and optical metallography were used to evaluate scaling of the core. Corrosion of the plate was evaluated by visual and metallographic means.

2.3 DESCRIPTION OF SPECIMENS

A single core, a HOTERV heat exchanger section, was used in all test runs. Fin samples were periodically removed for examination. The core was cleaned with a hot DIW rinse between groups of test runs. The other specimen tested was an inclined aluminum plate (Alloy 1100). New plates were placed in the CDL for every test run except one in which a long-term test run was desired. These plates were unanodized for the first four runs; thereafter, half of each plate was removed and anodized before testing. Both plate halves were tested simultaneously.

The specimen section contained the two test elements: the HOTERV test section, approximately 18 cm x 15 cm x 15 cm, and the reference plate of initially unanodized 1100 Al sheet, approximately 30.5 x 15 cm x 0.1 cm. The HOTERV specimen is a test section of a DCT element manufactured in Hungary (HOTERV Surface) provided to PNL by Babcock and Wilcox, U.S. licensee for HOTERV heat exchangers. The reference plate provides a simple surface geometry for comparison. The aluminum plate was provided by Reynolds Aluminum Co. The 1100 alloy was chosen for testing as it is similar to the composition of the aluminum of the HOTERV element and is in common usage. The alloy compositions are listed in Table 2-1 (12, 13).

Table 2-1

ALUMINUM ALLOY COMPOSITIONS (%)

	Minimum Aluminum	Maximum Trace Elements % by Weight					
		Si	Fe	Cu	Mn	Mg	Zn
HOTERV DCT element (12)	99.5	--	--	--	--	--	--
Aluminum Alloy EC* (13)	99.6	--	--	--	--	--	--
Aluminum Alloy 1050	99.5	0.25	0.40	0.05	0.05	0.05	0.05
Aluminum Alloy 1100	99.0	(1.0 Total)		0.20	0.05	--	0.10
Aluminum Alloy 5056	93.5	0.30	0.40	0.10	0.20	5.6	0.10

*EC = Electrical Conductor Grade.

2.4 TEST PARAMETERS AND CONDITIONS

The principal test parameters were the number of wet/dry cycles and the water composition or equivalent concentration factor. All other operating conditions (temperature, cycle time, and air velocity) were not varied, except as noted in Section 4 of this report for CDL Mod-2 (steady state).

2.4.1 Water Concentration

The water composition at the ACT site was analyzed and evaluated to determine the maximum concentration factor (5X) that is theoretically permitted without steady state scale formation being predicted by the Langelier or Ryznar indices (14, 16) (see Table 2-2). This determination is dependent on the Langelier index, which is based on data from scaling on continuously wetted surfaces. There are reservations about applying it to periodically deluged systems since it is applicable only during continuous deluge flow. Deposition due to cyclic drying will depend both on the precipitation of inverse solubility salts and dissolved solids in the residual water film which dries at the end of a cycle. The initial "startup" water composition for the CDL tests was formulated to simulate well water at the Kern ACT site at less than the maximum concentration factor.

Table 2-2

LANGELIER AND RYZNAR INDICES

Langelier index for waters in pH range of 6.5 to 9.5

$pH - pH_S = pH - pK_2 - pK_S\ pCa + pAlk$ = saturation index (I)

pH = actual measured value

pH_S = the pH at $CaCO_3$ saturation

pK_2 = neg log of second dissociation constant for carbonic acid (corrected for ionic strength and solution temperature)

pK_S = neg log* of solubility product for $CaCO_3$ (corrected as above)

pCa = neg log of molal calcium concentration

$pAlk$ = neg log of alkalinity expressed as equivalent ($CaCO_3$) per liter

Langelier index of zero (±0.5) implies that the water causes neither scaling nor corrosion

+ 1 implies scale formation

- 1 implies corrosive waters

Ryznar index

$2(pH_S) - pH = -2I + pH$ = stability index (R)

I = Langlier saturation index

Ryznar index of 6.5 ± 0.5 (6.0 - 7.0) is neutral

7 implies scale dissolved into solution

6 implies scale-forming components readily come out of solution

---

*Negative logarithm.

Once a water composition was selected from the permissible range, the pH was adjusted to correspond to a Langelier index near 0, so that the deluge water should neither cause deposits under steady-state conditions nor be corrosive. A pH of 8.5 was chosen because it is high enough to give reasonable values for the Langelier and Ryznar indexes (defined in Table 2-2), but it tends to minimize aluminum corrosion, which increases rapidly at high pH (>9). This pH (8.5) also requires minimal addition of sulfuric acid to this naturally alkaline water (pH 8.6 when unconcentrated).

Deionized water was provided automatically to make up evaporative losses during test runs. This deionized water was analyzed and the results are shown in Table 2-3. The use of DIW in the CDL to make up water lost by evaporation gives rise to the two CDL water concentration factor curves in Figure 2-7. The tests in the unrinsed mode were marked by a gradually decreasing TDS level as solids were removed from solution. The curve for the rinsed mode also decreases, but not as rapidly over the long term. It does, however, fluctuate slightly (<5%) within each cycle.

Table 2-3

DEIONIZED WATER COMPOSITION

Species	Concentration mg/ℓ
Al	0.1787
B	0.0044
Mg	0.0115
Na	0.4692
P	0.0525
Si	0.0354
As	0.0854
Cr	0.0110
Se	0.0995
Th	0.2271
Tl	0.0126
U	0.0080
All other metals	Not detected

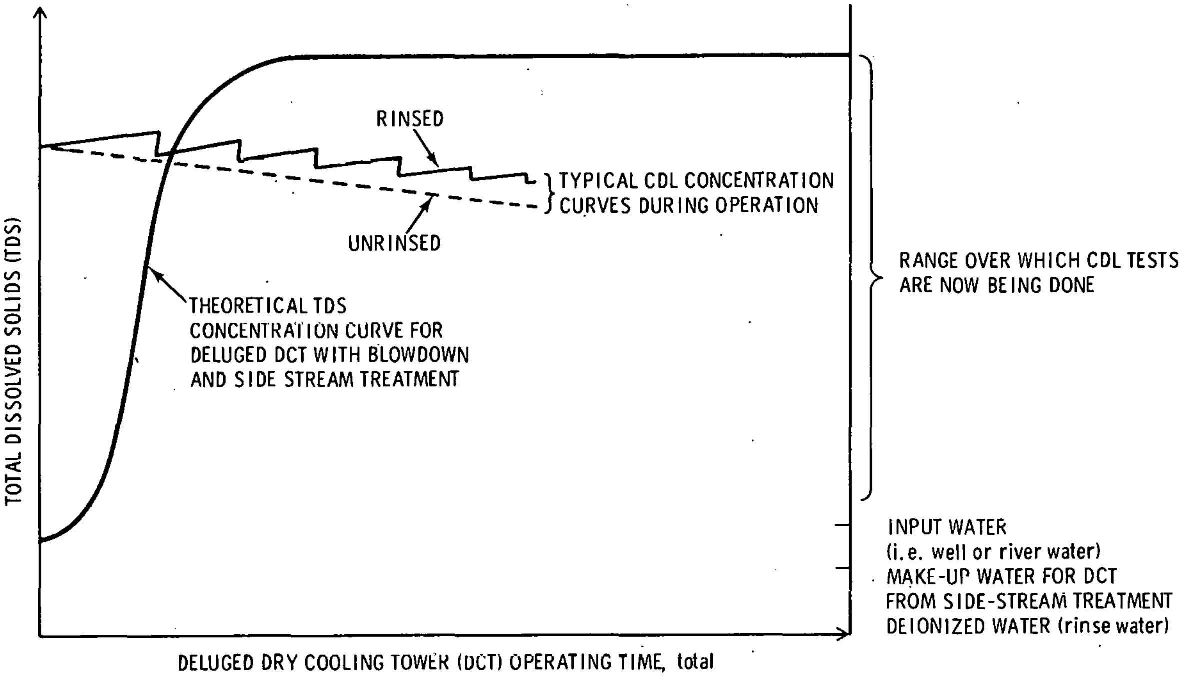

Figure 2-7. Concentration Curves

This occurs because the evaporative make-up is applied once each cycle as the specimen rinse water. Also shown in Figure 2-7 is the theoretical TDS concentration buildup for a deluged dry cooling tower operation with a side stream treatment unit.

Deluge water is simulated by multiplying the constituent concentrations from the analysis of the raw feed water used at the Kern power plant in Bakersfield, California, by a suitable concentration factor (2, 3 or 4) to simulate water concentration due to cycled usage (see Table 2-4). A charge balance was determined for the original analysis and the excess cationic charge is balanced with chloride ion. A calculation of solution saturation for $CaCO_3$ and $CaSO_4$ using standard Ksp values shows the 4X concentrated solutions to be slightly supersaturated. This is also reflected in the +0.4 Langelier Index at 4X.

Table 2-4

WATER COMPOSITION AT VARIOUS CONCENTRATION FACTORS

Constituent	Concentration, ppm *Kern Well Water Untreated	 **Kern 2X Acid Added	 **Kern 4X Acid Added
Na	35.0	70.0	140.0
Cl	9.5	19.0	38.0
SiO_2	17.4	35.0	70.0
Ca (as $CaCO_3$)	17.2	34.0	69.0
Mg (as $CaCO_3$)	2.8	5.6	11.0
SO_4	18.0	36.0	72.0
Alkalinity (as $CaCO_3$)	69.0	120.0	240.0
Total Dissolved Solids	142.0	300.0	650.0
Hardness (as $CaCO_3$)	20.0	40.0	80.0
pH	8.6	8.5	8.5
Langelier Index at 30°C	-0.2	+0.2	+0.4
Ryznar Index at 30°C	9.0	8.1	7.6

---

*As analyzed by Betz Laboratories.

**Theoretical.

Samples of the deluge water were taken periodically for a full analysis. Standard methods were used in evaluating these samples. For further details on sampling technique, see Appendix A. The analytical data from the deluge water analysis are presented in Table 2-5.

At least eight main factors potentially affect the deluge water chemistry:

1. Intentional addition of deionized water to maintain water volume.
2. Intentional addition of simulated deluge water to maintain approximate pH, conductivity and total dissolved solids levels
3. Sample temperature
4. Loss of dissolved constituents by deposition

5. Absorption of chemical species, such as CO_2 and particulate NaCl or SiO_2, from air

6. Gain of aqueous constituents due to corrosion of test specimens and test apparatus

7. Sample timing with relationship to deluge cycle (samples are not always taken at the same point in the deluge cycle)

8. Apparatus failures such as recirculating pump failure, thermocouple failure, valve failure or heater malfunctions.

Known effects upon water chemistry are noted directly on the graphs of pH-conductivity versus time appearing in Appendix A.

Several tests show a marked drop of pH and conductivity with time which may be caused by two related phenomena. As deposition occurs carbonate is involved in the equilibration:

$$CO^{2-}_{3(aq)} + Ca^{2+}_{(aq)} \rightleftharpoons CaCO_{3(s)}$$

Thus, absorption of CO_2 from the air to replace that lost to deposition as $CaCO_3$ will cause the pH to drop as this equilibration proceeds:

$$CO_{2(g)} + 2OH^{-}_{(aq)} \rightleftharpoons CO^{2-}_{3(aq)} + H_2O$$

These equilibria apply principally to steady state deposition conditions, and less to cyclic deluged conditions. However, loss of ions from solutions, as in the deposition of $CaCO_3$ would cause the conductivity to drop as was observed. Note that in tests 2 and 3A, Ca levels have dropped in spite of the addition of deluge water near the end of the run. Also note that the pH is still high enough throughout the test to prevent dissolution of $CaCO_3$ precipitates. Test 3B analytical results differ from 2 and 3A, probably because of the continuous slow addition of simulated deluge water to the system. The overall results from all runs seem to signal no particularly significant trends in the water chemistry, despite the variation in the Langelier index in each data run. The index values shown in Table 2-5 do vary from optimum, due to composition changes as deposition occurs.

2.4.2 Operating Conditions

Some experimental parameters were constants for all cyclic test runs. In the CDL, these constant parameters are the specimen configuration, the air velocity, the

Table 2-5

DELUGE WATER COMPOSITION DURING CYCLIC DATA RUNS

Run Number	2	2	3A	3A	3B	3B	3B	3B	4A	4A	4A
Sample Number	4-19	4-27	5-11	5-19	5-26	6-1	6-6	6-12	7-14	7-19	7-21
Concentration Factor[a]	4X	4X	2X	2X	2X	2X	2X	2X	3X	3X	3X
Running Time (Hours)	0	188	0	190	72	312	412	570	0	100	122
Sample Temp (°C)	42	40	39	30	38	39	36	31	31	29	32
pH (8.5 nominal)	8.65	8.66	8.50	8.20	8.55	8.43	8.32	8.17	8.40	8.04	8.81
Conductivity (μmho/cm)	825	950	480	480	860	1090	895	765	715	320	425
-CO_3(mg/ℓ)	d	8.6	1.9	0	0	0	0	0	7.7	0	28.3
Alkalinity											
-HCO_3(mg/ℓ)	103	95.5	76	55	74.4	85.9	72.6	65.1	179.0	97.3	293.4
TDS (mg/ℓ)[b]	401	498	253	268	450	600	557	533	441	221	379.5
SiO_2 (mg/ℓ)	20	25	26.0	4.0	12	2.7	3.3	12	13	4.0	22.0
Al (mg/ℓ)	1.0	1.0	1.0	1.1	1.8	4.9	3.8	1.6	0.25	1.07	0.09
Ca (mg/ℓ)	34	5.2	8.0	2.7	3.7	3.2	3.9	5.9	8.74	5.57	4.68
Fe (mg/ℓ)	0.25	0.1	0.08	0.05	0.02	0.05	0.08	0.03	0.03	0	0
Mg (mg/ℓ)	1.28	1.1	0.9	0.3	0.94	0.55	0.43	1.1	1.57	0.75	1.92
Na (mg/ℓ)	150	170	59	68	143	203	173	177	148	68	107
Cl (mg/ℓ)	46.3	50.0	20.0	26.2	43.7	61.3	59.2	54.4	41.1	20.4	33.1
SO_4 (mg/ℓ)[c]	180	190	82.0	120	180	240	240	240	180	90	170
Langelier Index	+1.1	+0.2	+0.2	-0.8	-0.2	-0.3	-.05	-0.6	+0.3	-0.5	+0.7
Ryznar Index	6.4	8.2	8.0	9.9	9.0	9.1	9.3	9.4	7.8	9.0	7.3

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[a] Concentration factor = factor by which original Kern untreated supply water is multiplied to obtain more concentrated deluge water.

[b] Total dissolved solids.

[c] Before addition of H_2SO_4 to adjust pH to 8.5.

[d] Final concentration dependent upon final SO_4 concentration.

Table 2-5

(contd)

Run Number	4B	4B	4B	5A	5A	5A	5B	5B	5B	5B	5B	5B
Sample Number	8-4	8-9	8-12	8-21	8-25	8-29	8-30	9-1	9-6	9-8	9-11	9-15
Concentration Factor[a]	3X	3X	3X	4X	4X	4X	4X	4X	4X	4X	4X	4X
Running Time (Hours)	0	119	194	0	93	189	0	49	169	217	289	385
Sample Temp (°C)	40	39	38	38	37	38	40	39	35	36	35	37
pH (8.5 nominal)	8.74	8.14	8.50	8.52	8.27	7.51	8.20	8.18	8.15	8.21	8.13	7.44
Conductivity (μmho/cm)	1200	320	860	720	590	600	800	850	1000	1000	500	260
- CO_3(mg/ℓ)	0.8	0	46	0	0	0	26.0	0	2.6	0	0	0
Alkalinity												
- HCO_3(mg/ℓ)	72.0	39.3	41	42.3	20.4	55.5	13.2	52.9	41.6	27.8	29.1	7.9
TDS (mg/ℓ)[b]	650	168.5	406	411	286	298	416	366	731	516	232	113
SiO_2 (mg/ℓ)	38	7.0	9	4.6	5	4	18	7	4.3	14	11	4
Al (mg/ℓ)	0.02	0.51	0.91	0.57	1.67	0.85	0.7	0.8	0.84	0.33	1.02	0
Ca (mg/ℓ)	13.09	4.87	4.5	16.92	9.61	10.32	13.64	10.45	17.60	13.20	13.71	8.94
Fe (mg/ℓ)	0.12	0.02	0.01	0.25	0.04	0.04	0.05	0.10	0.04	0.06	0.03	0.03
Mg (mg/ℓ)	3.36	0.71	0.97	2.21	0.88	0.77	1.49	0.94	2.59	1.21	0.81	0.48
Na (mg/ℓ)	223	50	129	106	92	92	132	118	246	169	75	39
Cl (mg/ℓ)	63.3	20	40	33.3	23.7	27.5	37.5	35	73.3	53.3	21.7	7.5
SO_4 (mg/ℓ)[c]	240	60	170	160	120	130	140	280	260	190	120	50
Langelier Index	+0.5	-0.6	+0.1	+0.1	-0.5	-0.8	-0.1	-0.2	-0.2	-0.5	-0.4	-1.7
Ryznar Index	7.7	9.4	8.2	8.2	9.4	9.2	8.3	8.6	8.6	9.2	89	11.0

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[a] Concentration factor = factor by which original Kern untreated supply water is multiplied to obtain more concentrated deluge water.

[b] Total dissolved solids.

[c] Before addition of H_2SO_4 to adjust pH to 8.5.99

test specimen temperature setting, the deluge water temperature setting and flow rate, and the deluge cycle length. The only experimental variables are the initial water composition, its Langelier index, and the run time.

The temperature settings for the specimens and the deluge water were based on a "typical" dry-cooled operating environment. These conditions were nominally a deluge water temperature of 32°C and a dry specimen temperature of 60°C. Deluging altered specimen temperature as shown in Figure 2-8. No attempt was made to control the inlet air temperature since drying was all that was desired. Ambient air temperature varied from about 16°C to 27°C. Air velocity past the test specimens was selected on the basis of the preliminary results of heat transfer studies on this type (HOTERV) heat exchanger. The studies were part of the Water-Augmented Test Apparatus (WATA), a large-scale loop study comparing heat transfer characteristics of several dry-cooled heat exchangers. These studies are to be published separately in PNL-2746.

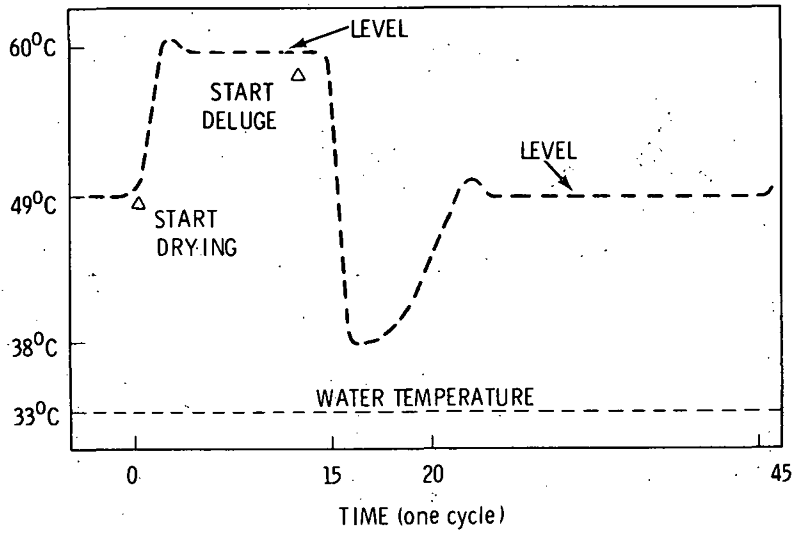


Figure 2-8. Specimen Temperature Variations Over One Deluge Cycle (45 min)

Section 3

DISCUSSION OF CORROSION/DEPOSITION LOOP (CDL) CYCLIC RESULTS

Deposition and corrosion product formation on heat exchanger surfaces will inhibit heat transfer and alter cooling water composition. Runs 1 through 5 (Table 3-1) examine deposition and corrosion in cyclic operation caused by exposure to water of selected composition.

A summary of run conditions is as follows:

- Run 1 (at a concentration factor of 4X) was terminated after 75 cycles, which corresponds to 2-1/2 months of cyclic deluge operation.
- The scheduled 250 cycles could not be completed because of a temperature excursion that warped the plate specimen, causing nonuniform heating and water dispersion on the plate surface. The temperature excursion did not affect the HOTERV specimen.
- Run 2 was also at a factor of 4X concentration but ran the full 250 cycles as programmed.

Table 3-1

CYCLIC RUN DATA SUMMARY

Run No.	Concentration Factor	Run Length	*Remarks
1	4X	60 cycles	plate was warped by temperature excursion
2	4X	250 cycles	
3A	2X	250 cycles	1000 cycles total
3B	2X	750 cycles	
4A	3X	220 cycles	repeated due to equipment failure
4B	3X	250 cycles	
5A	3X	250 cycles	rinsed, 750 cycles total
5B	3X	500 cycles	

---

*All other run parameters were constants: specimen dry temperature - 60°C, deluge water temperature - 32 to 40°C, deluge flow rate - 4 ℓ/min, deluge water pH - 8.5, air velocity - 1 m/sec, ambient, and cycle length - 45 min (30 min deluged - 15 min dry).

- Run 3 was at a concentration factor of 2X but was a longer run, extending to 1000 cycles, with weighing and inspection after 250 cycles.
- Run 4 at a concentration factor of 3X was repeated after an equipment malfunction permitted all the deluge water to evaporate. The plate specimen for this run was in two portions, with one half bare metal as in previous runs, while the remaining half had been anodized in oxalic acid (Appendix B).
- Run 5 was at a concentration factor of 4X and differed from the previous runs in that the specimens were rinsed with deionized water after each deluging. This run was in two parts, with a weighing and examination at 250 cycles and again at 750 cycles at the end of the test run.

3.1 HOTERV HEAT EXCHANGER

Primary data to date consist of weight changes for the HOTERV heat exchanger and plates at three concentrations (2X, 3X, 4X) and four run lengths (60, 250, 750 and 1000 cycles). Additional information was obtained by x-ray diffraction, scanning electron microscopy (SEM) and optical metallography, supplemented by visual observations of the specimen surfaces. Graphs for the primary data are presented as Figures 3-1 through 3-4, for the HOTERV core.

3.1.1 Weight Gains, Unrinsed Data Runs

The HOTERV core gained weight from deposition in all data runs, with little surface corrosion observable. The weight gain was linear with concentration factor for a fixed number of cycles (Figure 3-1) and linear with cycles at all fixed concentration factors, i.e., 2X and 4X (Figures 3-2 and 3-3). Figure 3-4 shows all the unrinsed core data, including zero point, plotted with a normalized factor (composed of cycles times concentration factor) against weight change per unit area as $mg/(dm)^2$. Eight data points are shown forming a reasonably linear array, passing through zero as required.

The linearity of this relationship implies that deposition rate is relatively constant by whatever mechanism is responsible. However, the interpretation is not completely quantitative on an area basis because the core surface area was not entirely wetted; therefore, some of the deposition must result from splashing and then drying on the unwetted surfaces. Steady-state deposition may be considerable as will be discussed in Section 4.0.

Calculations are further complicated because it is uncertain how much of the dried deposit redissolves when the deluge resumes. Visual observations reveal that the deposition is not uniform (Figure 3-5) but is concentrated around the surfaces

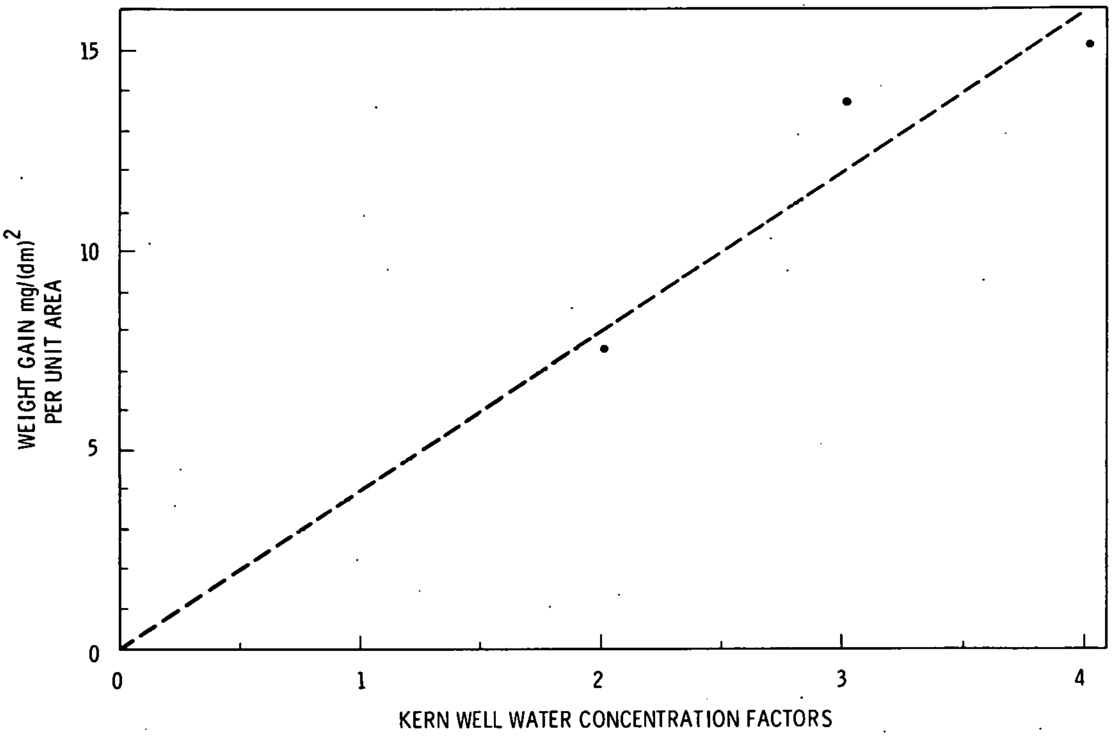


Figure 3-1. Weight Gain Versus Concentration Factor at Constant Number of Cycles (250)

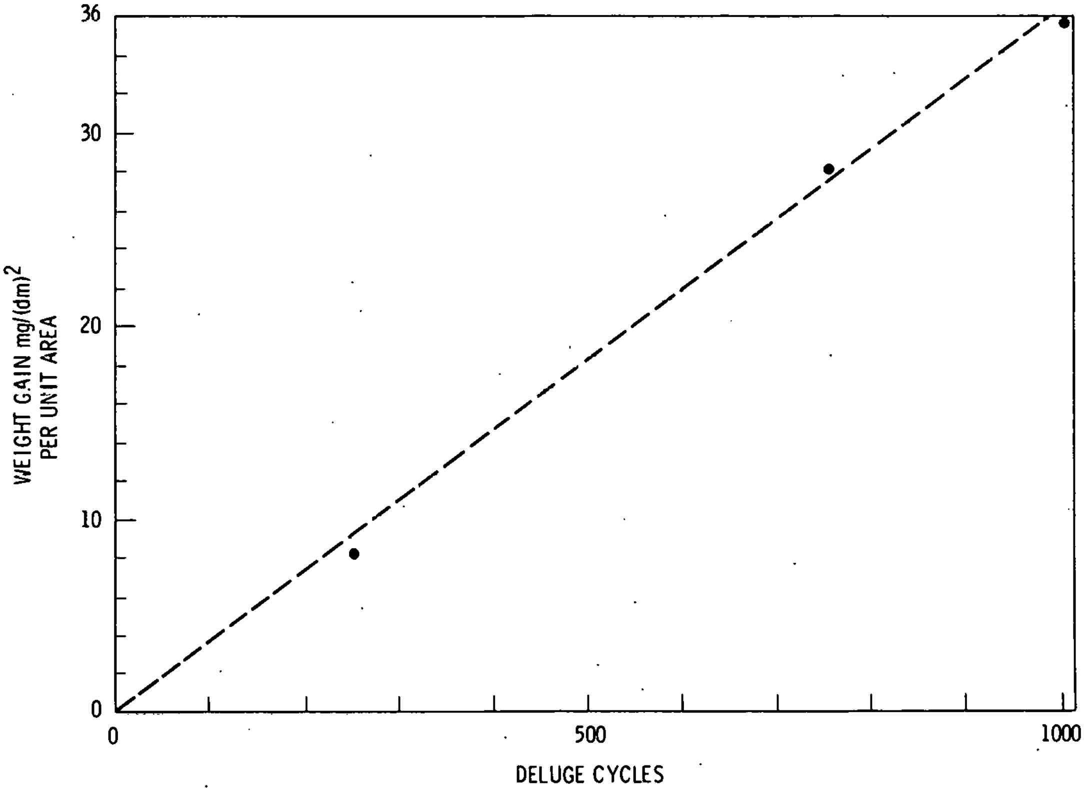


Figure 3-2. Weight Gain Versus Deluge Cycles at Constant Kern Water Concentration Factor of 2X

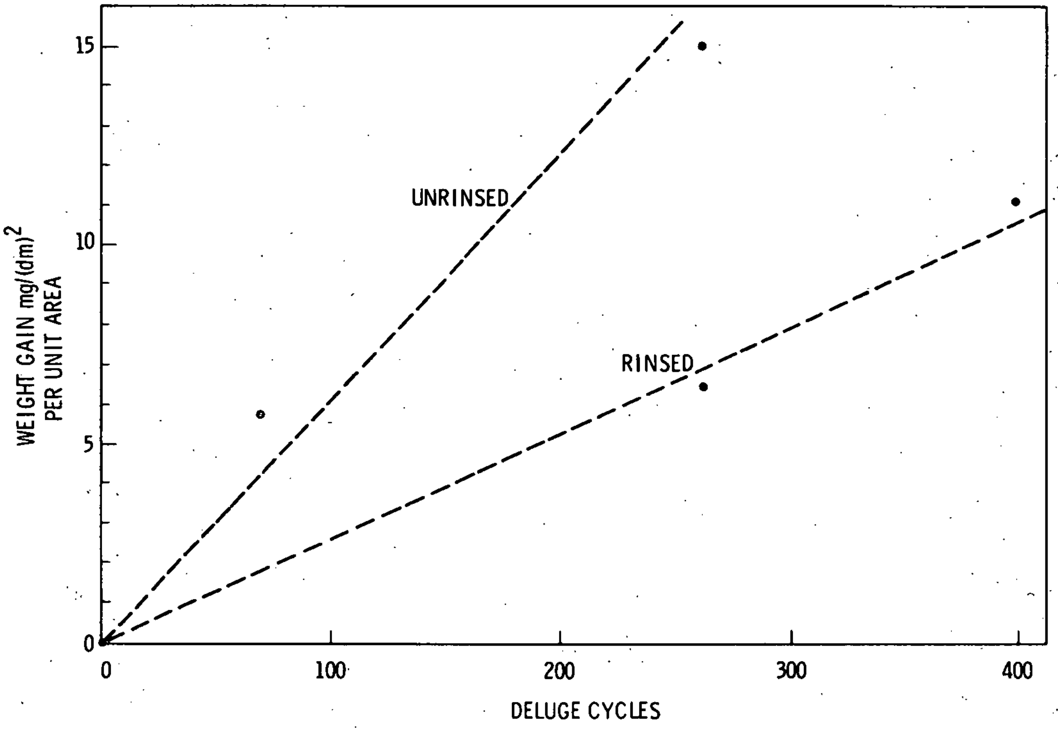


Figure 3-3. Weight Gain Versus Deluge Cycles at a Constant Kern Water Concentration Factor of 4X

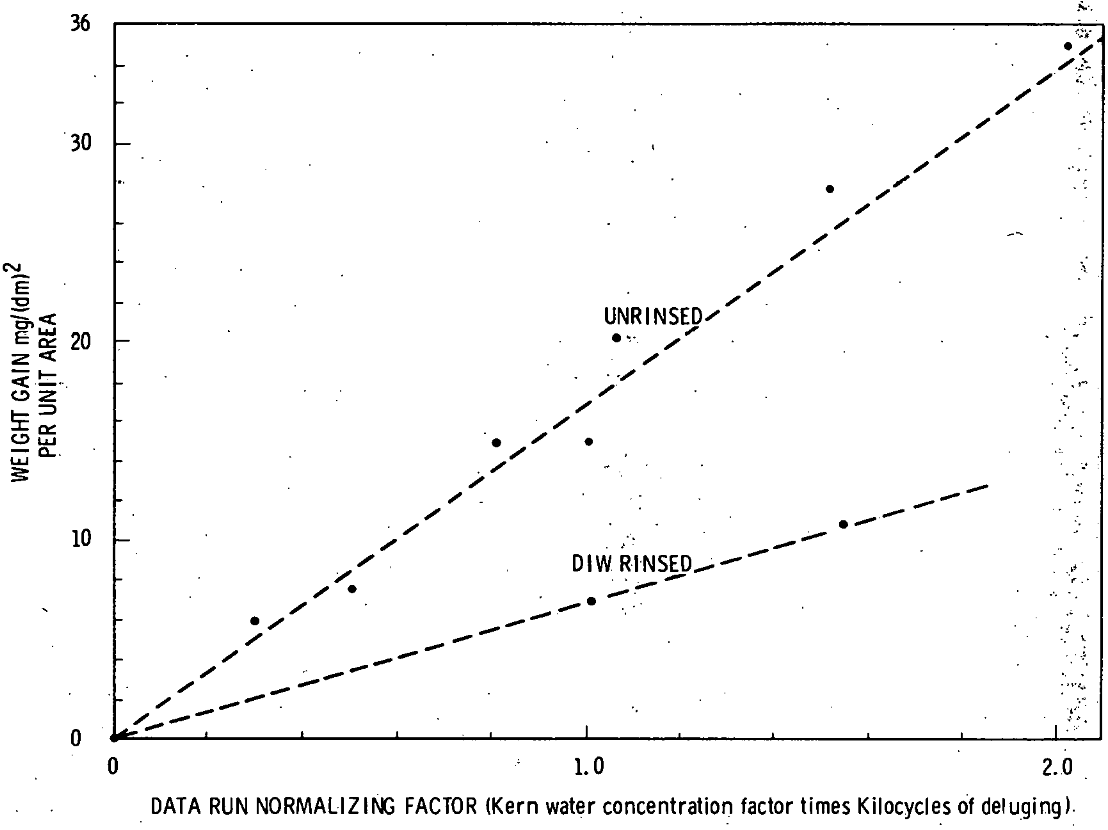
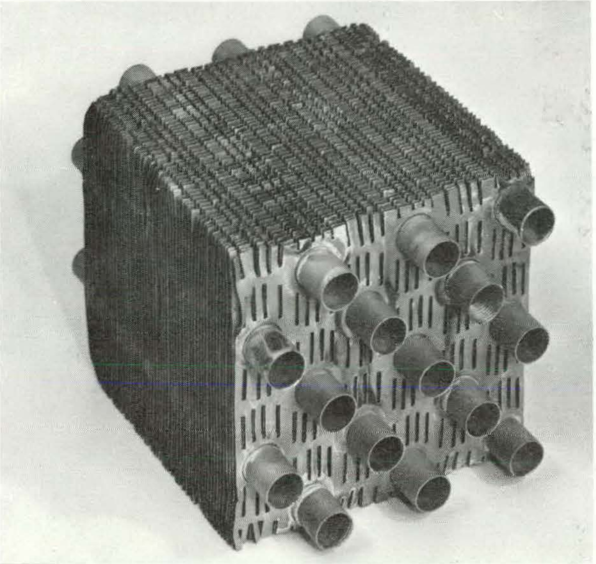
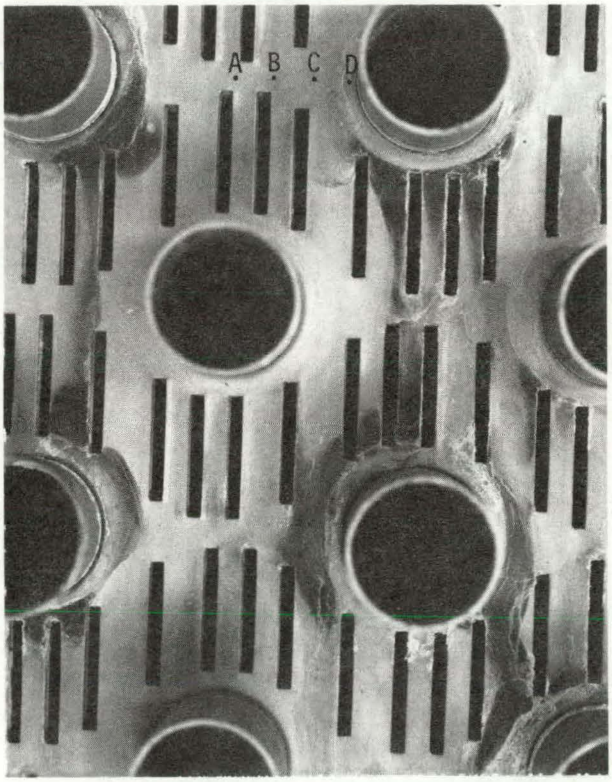


Figure 3-4. Weight Gain Versus Data Run Normalizing Factor for Core Data



0.3x*(#PNL 78d 014 - 8)

a) HOTERV DCT Element After Unrinsed Data Run



Air Flow
Deluge Flow

b) "Stains" and Deposition are evident on surface after an unrinsed data run.

1.2x*(#H-1-3x-A)

Figure 3-5. Macrographs of the HOTERV DCT Element

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*Please note that the illustrations on this page have been reduced 10% in printing.

nearest the heated tubes, as would be expected (17). Other tests in the WATA program have indicated that these are regions of higher fin temperature and that the bulk of the heat transfer occurs there. In a deluged (and irregularly wetted) system these are the areas which would dry most rapidly and be subject to the greatest amount of steady-state deposition during deluging.

Figure 3-6 is a series of four micrographs which demonstrates deposit buildup in the vicinity of a heated tube. The slots in the HOTERV fins also had some effect on deposition patterns as Figures 3-7 and 3-8 show. The slots appear to cause some turbulence in the flowing deluge water.

Scanning Electron Microscope (SEM) analysis of the deposition shows principally calcium and silica. Some silica may possibly arise from airborne sand particles carried into CDL. Magnesium silicate is known to precipitate out even when the Langelier and Ryznar indexes do not predict scaling in the system, (14, 18, 19) particularly when the silica value is high (100 mg/ℓ), as it is at Kern and as it often was in the CDL for several of the test runs. SEM microprobe analysis has detected some magnesium in some of the HOTERV deposits, but is inconclusive as the Mg content was low.

Metallography of the HOTERV specimens reveals numerous but very small pits (Figure 3-9). Unfortunately, the total time (41 days or 1,310 cycles) during which the specimen has been tested was insufficient to draw any meaningful conclusions on rate of pitting or pit growth kinetics. But a comparison of a second HOTERV sample, taken from a specimen deluged less than 100 times over several months of primarily dry operation, and then deluged only with deionized water, shows much less pitting (Figure 3-10a). This sample had a deposition layer. It is assumed that this deposition originated from airborne matter, as it is rich in silica, but calcite is also observed and as yet its presence is not adequately explained.

The anodized film on the HOTERV core surfaces is about 8 μm thick. This anodized layer is formed by a M.B.V.* process and is rich in chromium, a corrosion inhibitor (20). However, the anodized layer appears to have numerous (ca. $10^5/cm^2$) pores that are 5 μm in diameter. It appears that some of these pores are large enough to penetrate the anodized layer completely and could be the primary cause of the observed pitting (Figure 3-10b).

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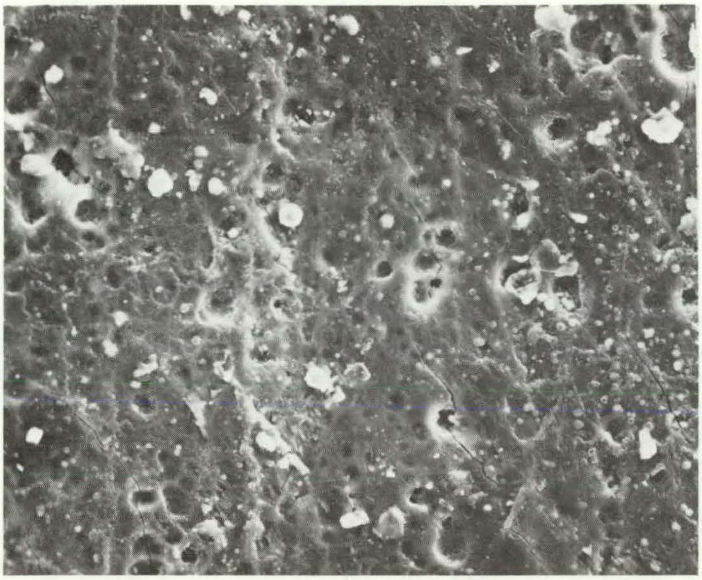
*A commercial chemical oxidation process.

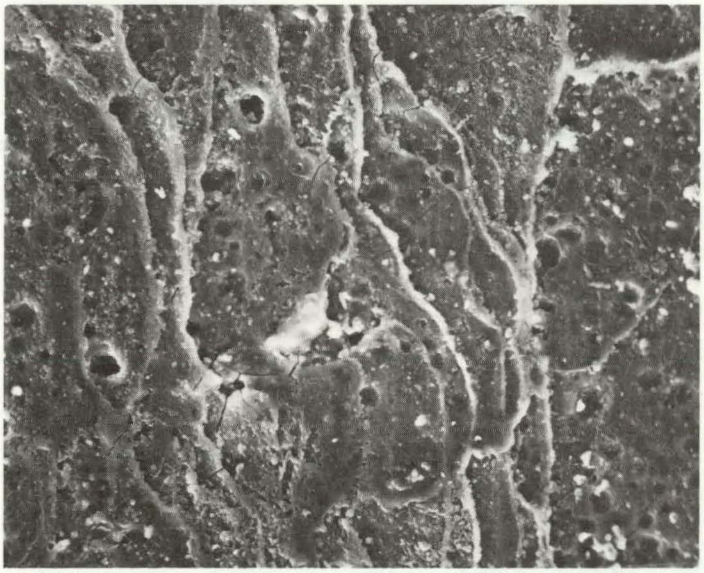


SEM microprobe analysis normalized to aluminum: full surface scan

Si/Al	Ca/Al	Cr/Al	Cl/Al
0.37	0.13	0.37	0.05

Na/Al	S/Al	Fe/Al
	0.04	0.04

a) Fin Surface Away From Heated Tube, (pt. A on Figure 3-5b) Little Deposit



SEM microprobe analysis normalized to aluminum: full surface scan

Si/Al	Ca/Al	Cr/Al	Cl/Al
0.41	0.12	0.38	0.05

Na/Al	S/Al	Fe/Al
0.02	0.05	0.05

b) Closer to Tube, (pt. B on Fig. 3-5b) Ripples of deposit formation

300x* (#B-15, 942)

Figure 3-6. Series of Micrographs Showing the Progressively Heavier Deposits on Fin Surface by Deposits on Nearing a Heated Tube

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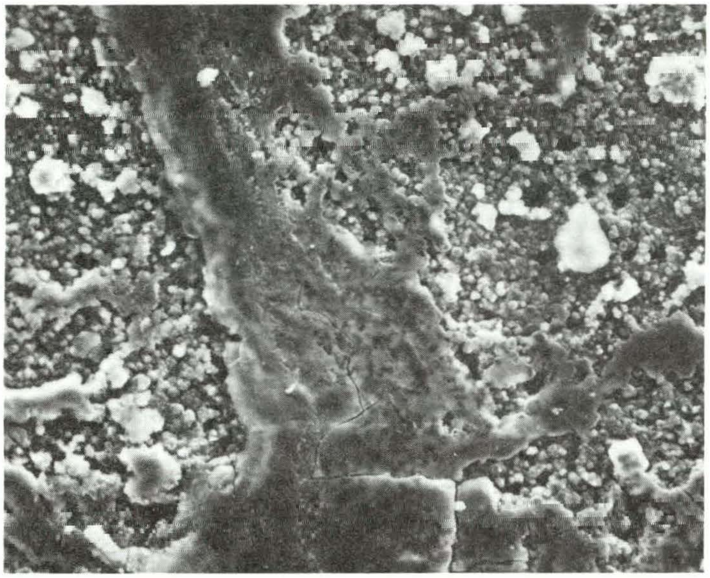
*Please note that the illustrations on this page have been reduced 10% in printing.

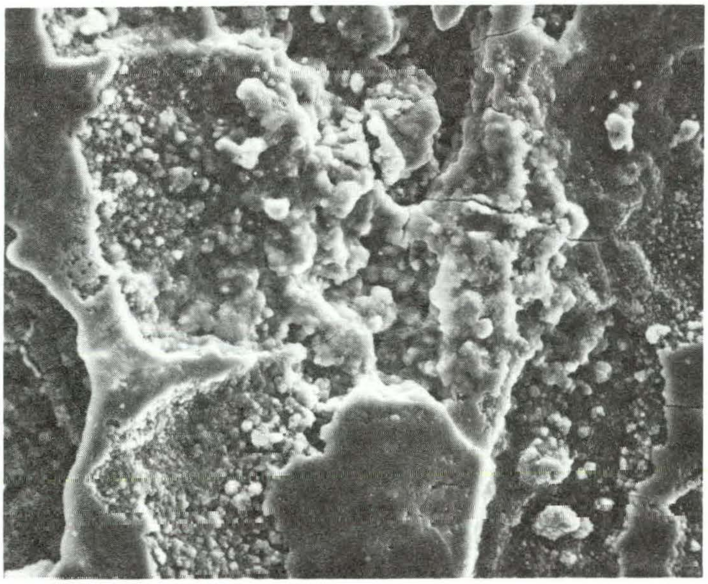


SEM microprobe analysis normalized to aluminum: full surface scan**

Si/Al	Ca/Al	Cr/Al	Cl/Al
3.51	0.52	0.49	---
Na/Al	S/Al	Fe/Al	
0.02	0.11	0.10	

c) Nearer Tube, pt. C on Fig. 3-5b) Deposits cover much of surface.

300x* (#B-15, 941)*



SEM microprobe analysis normalized to aluminum: full surface scan

Si/Al	Ca/Al	Cr/Al	Cl/Al
2.97	3.79	0.29	0.21
Na/Al	S/Al	Fe/Al	
0.13	0.29	0.24	

d) Next to the Tube, (pt. D on Fig. 3-5b) Deposits cover nearly all of surface.

300x* (#B-15, 939)

Figure 3-6. (contd)

*Please note that the illustrations on this page have been reduced 10% in printing.

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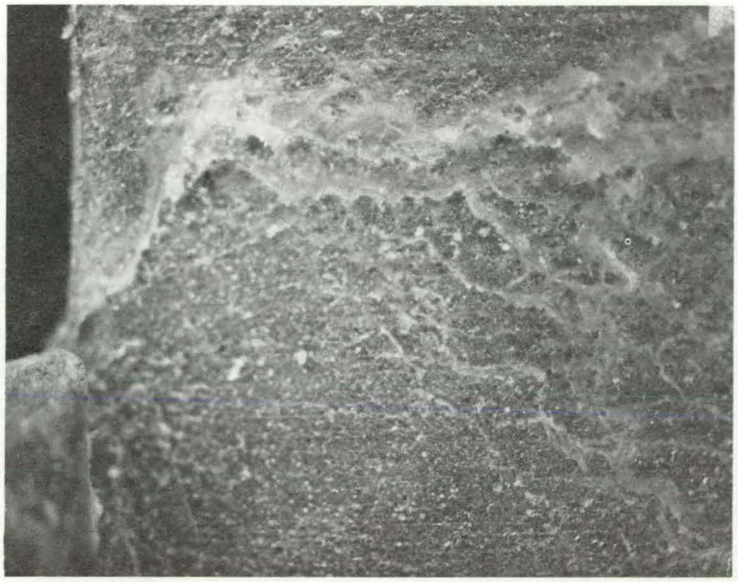
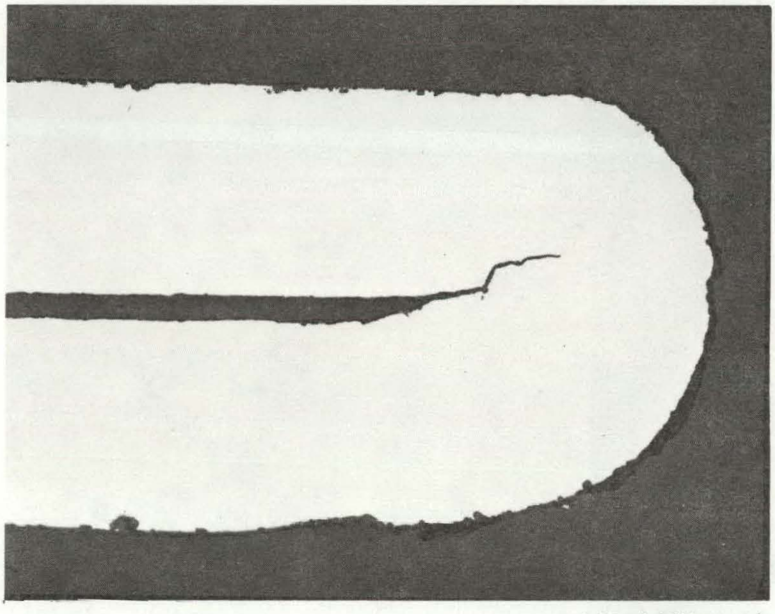
*Micrograph identification number.

**Numbers represent relative comparison of amount of indicated species to amount of aluminum.



45x* (#4N 965B)

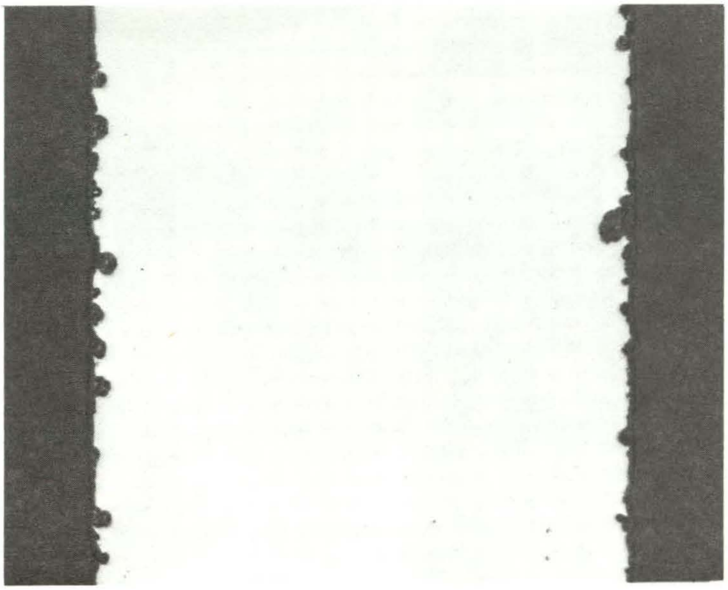
Figure 3-7. Typical Deposition Pattern - Associated with Finned Surfaces Slots on HOTERV



100x* (#H-3-3)

Figure 3-8. Micrograph of Folded Metal Slot on HOTERV Core (Note thicker deposition on fin leading edge. Crack origin is unknown.)

*Please note that the illustrations on this page have been reduced 10% in printing.



a) Section of fin from
HOTERV Aluminum core
from CDL

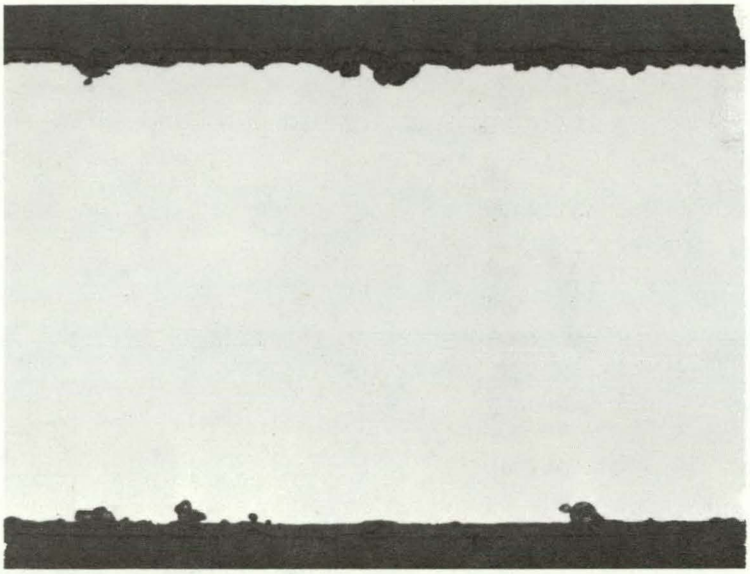
250x* (#4N-971B)

b) Enlargement of
Typical Pit Area

3,000x* (#B-15, 950)

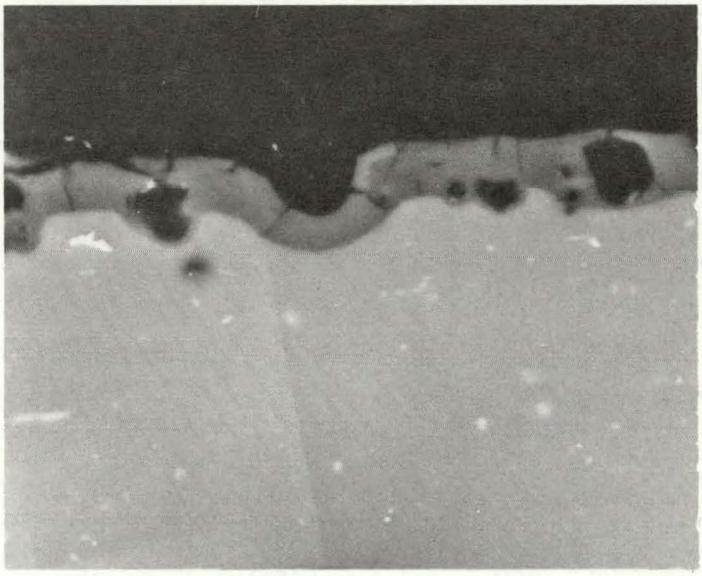
Figure 3-9. Micrograph of a Cross Section of a HOTERV Aluminum Heat Exchanger Fin After ∿300 Cycles of CDL Testing

*Please note that the illustrations on this page have been reduced 10% in printing.



200x* (#4N1353B)

a) Typical HOTERV Fin Section



1000x* (#B-16, 096)

b) SEM Micrograph of HOTERV Fin Section

Figure 3-10. HOTERV Aluminum Fin Sections Showing Anodizing Thickness and Surface Irregularities

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*Please note that the illustrations on this page have been reduced 10% in printing.

3.1.2 Rinsed Data Run

Rinsing the deluge water from specimen surfaces with deionized water at the end of the deluge cycle significantly reduced the deposition rate on both the HOTERV and plate specimens. For comparison, the curve for the rinsed case appears in Figure 3-4 with the earlier unrinsed deposition data. The rinsing reduced the deposition rate by approximately a factor of three.

This observation supports the previous conclusion that in these early cyclic runs deposition was due partly to drying of the water film left behind on the specimens after each deluge cycle was terminated. The amount of rinse for each cycle is governed by the evaporative loss in the loop for each cycle. Thus, the rinse time in the loop is short (about 15 sec) for each cycle.

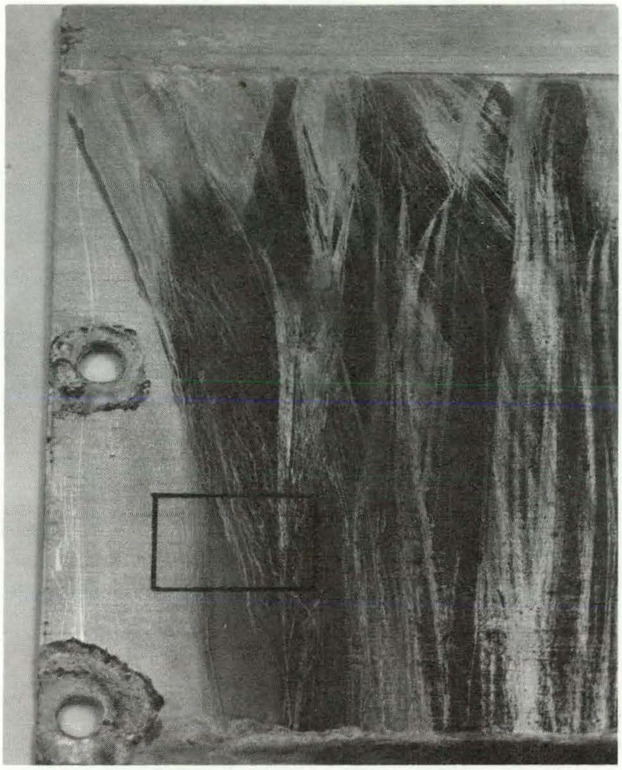
This would seem to be sufficient to completely remove the deluge water and may account for the lowered deposition rate. It is possible that steady-state solubility-induced deposition is occurring and is responsible for the remaining observed weight gain, though this is not predicted by Langelier or Ryznar indices.

3.2 PLATE SURFACES

The plate specimens were 1100 alloy aluminum and were 30.5 cm x 15 cm x 0.1 cm in size. Data runs 4 and 5 employed two specimens that were half as long as the earlier single specimen. These "split" plates had one section unanodized as before and the other half was anodized; except in run 5B where both pieces were anodized but one was sealed in a K_2CrO_3 solution attempting to produce an anodized layer rich in chromium similar to the anodized layer in the HOTERV specimens. There were no significant changes in the corrosion and deposition results that could be attributed to the K_2CrO_2 seal of this one run compared to the standard boiling water seal of the other runs.

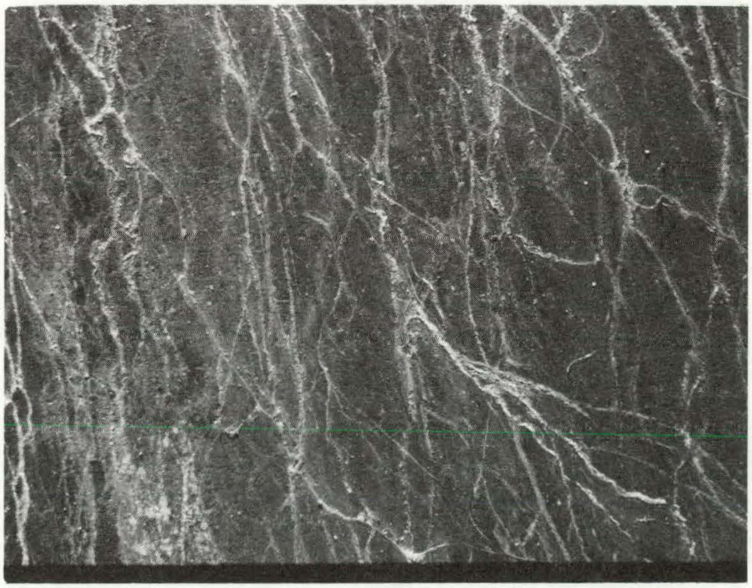
3.2.1 Unanodized Specimens

The early weight data from the unanodized (bare) plate specimen lacked consistency. The weight changes seemed to be nearly random, positive or negative, as corrosion and deposition each masked the other's singular effects. Figure 3-11 is a series of progressively higher magnifications of the same specimen after 1000 cycles during a 32-day run at 2X water concentration. The light colored areas are deposition and the dark areas are thin films of corrosion product. Figure 3-12 is a micrograph composite that shows a typical section through this specimen. It reveals the non-uniform deposition, the thin corrosion layer



a) Typical corrosion/deposition film on aluminum plate specimen

0.75x*(#PNL-78d 014-2)



b) Close-up of corrosion/ deposition film shown in box in figure above

12x*(#4N 963B)

Figure 3-11. A Series of Progressive Close-ups of Corrosion/Deposition Film on Aluminum Plate at 2X for 1000 Cycles

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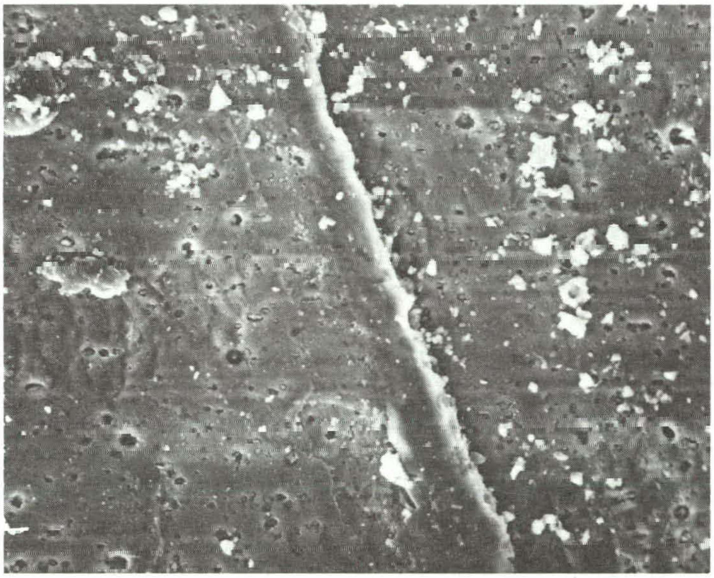
*Please note that the illustrations on this page have been reduced 10% in printing.

45x* (#4N 963D)

c) Thin film corrosion areas are located between deposition ribbons

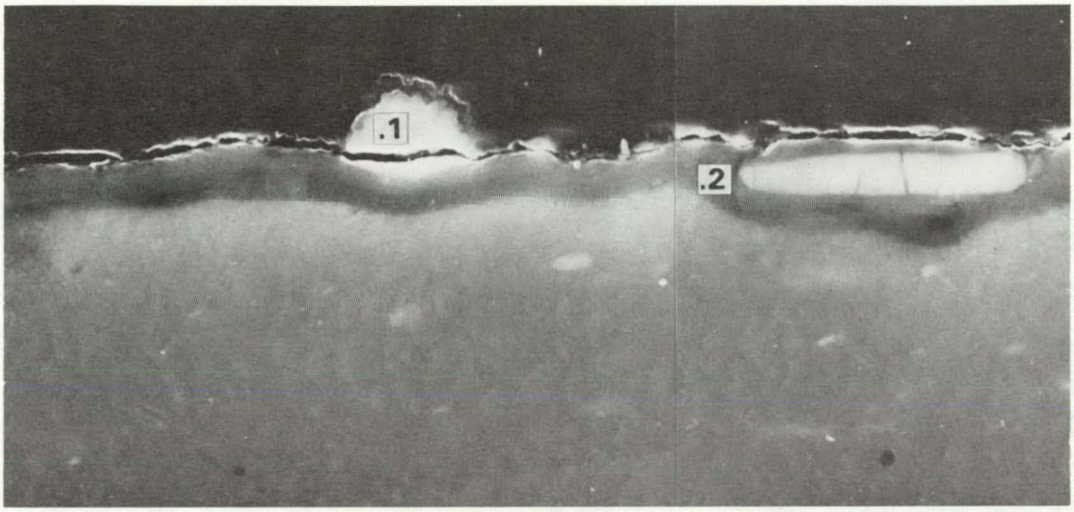


300x* (#B-15, 947)

d) SEM Micrograph of Deposition Ribbon

Figure 3-11. (contd)

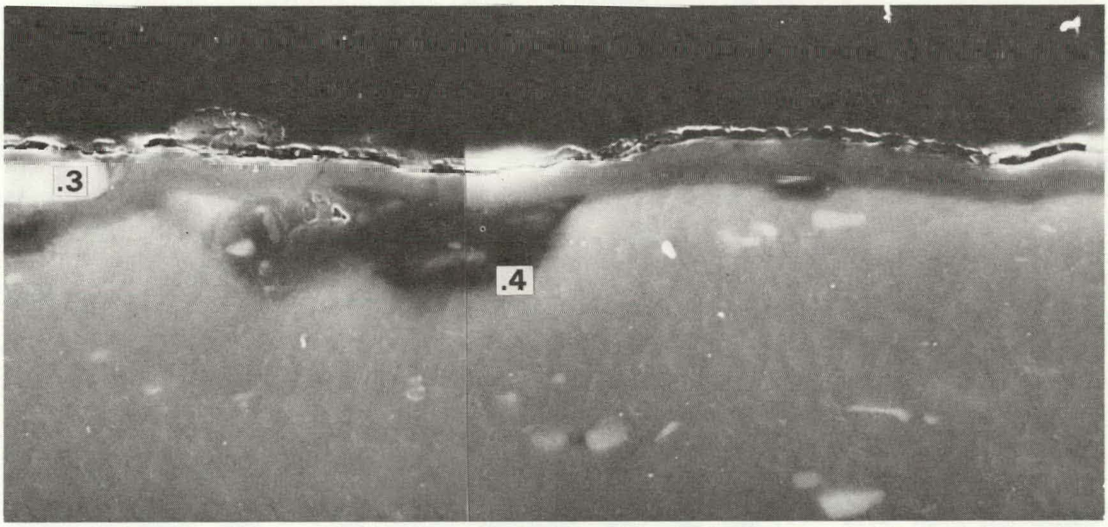
*Please note that the illustrations on this page have been reduced 10% in printing.



A

3000 x*(#'s B-15, 969-71)

	Si/Al	Ca/Al	Cr/Al	Cl/Al	S/Al	Fe/Al	( )/Al
pt 1	0.54	3.83	0.07	0.15	0.20	0.05	0.10(Mg)
pt 2	0.33	0.08	0.07	0.05	0.05	0.03	0.07(K)



A'

Points A and A' match

	Si/Al	Ca/Al	Cr/Al	Cl/Al	S/Al	Fe/Al	( )/Al
pt 3	0.16	0.05	0.02	0.04	0.03	0.25	0.04(Cu)
pt 4	0.06	10.03	0.02	0.02	0.01	0.03	--

SEM microprobe analysis was done at the points numbered 1 to 4 on the above micrographs. The data are presented in this figure and on the following page, normalized to aluminum.

Figure 3-12. A Series of Micrographs Showing a Typical Section of an Unanodized Aluminum Plate After 1000 Cycles of Unrinsed Running Time at 2 Concentration Factors. (Cross section taken along the bottom edge of the box shown in Figure 3-11a.)

*Please note that the illustrations on this page have been reduced 10% in printing.

prevalent over much of the surface and shows a typical pit. These pits were not numerous but some are beginning to show advanced development as Figure 3-13 reveals. A section through a deposition "ribbon" and SEM microprobe analysis (Figure 3-14) shows a calcium-rich deposit, overlaid by a second layer of mixed composition of principally Si and lesser amounts of Ca and K.

Figure 3-15 is a comparative sequence of two micrographs of the same area. The second photo is after the specimen has been etched. The corrosion has the appearance of subsurface attack observed by Johnson (6), resembling intergranular corrosion which could result in disintegration of the alloy and loss of strength.

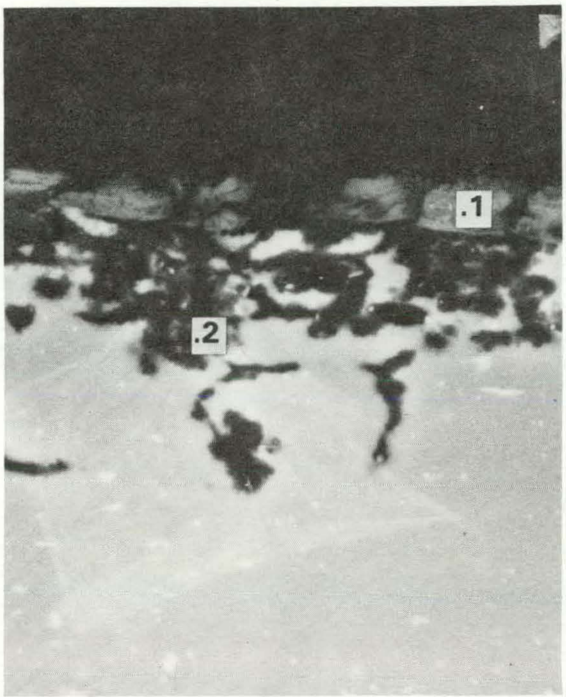
3.2.2 Deposition on Anodized Versus Unanodized Plate Specimens

In an effort to relate the HOTERV and plate data to each other and to investigate the effects of anodizing further, the plate was split. One half was exposed as anodized (Appendix B); one half was exposed simultaneously unanodized. A metallographic section (Figure 3-16) shows the thickness and uniformity of this anodized layer. Figure 3-17 shows the effect of anodizing on the corrosion/deposition that was previously typical for these specimens. Very little corrosion is observable and the deposition caused a definite weight gain. The anodized layer differed from the HOTERV surface in that the pores were fewer and smaller; the layer is lacking in Cr and is thicker. Whether it is more resistant to pitting than the HOTERV surface will be determined by subsequent investigations.

3.2.3 Rinsed Versus Unrinsed Weight Changes - Plate Specimens

In the first four runs, the deluge water film was allowed to remain on the plate specimens when the drying cycle started. Final weight changes were sometimes negative because corrosion-induced weight loss overshadowed deposition. However, visual observations confirmed that deposition was occurring on the plates.

The fifth run provided partial removal of the deluge water from the specimen surface by a 15 sec rinse with deionized water. This led to a substantial reduction in weight gain by a factor of one-sixth on sequential specimen plates. Additionally, visual comparison of the unanodized halves from the rinsed run and the previous similar unrinsed run also showed that the corrosion layer was thinner on aluminum surfaces which had been rinsed. Also, deposition was less on all rinsed pieces.

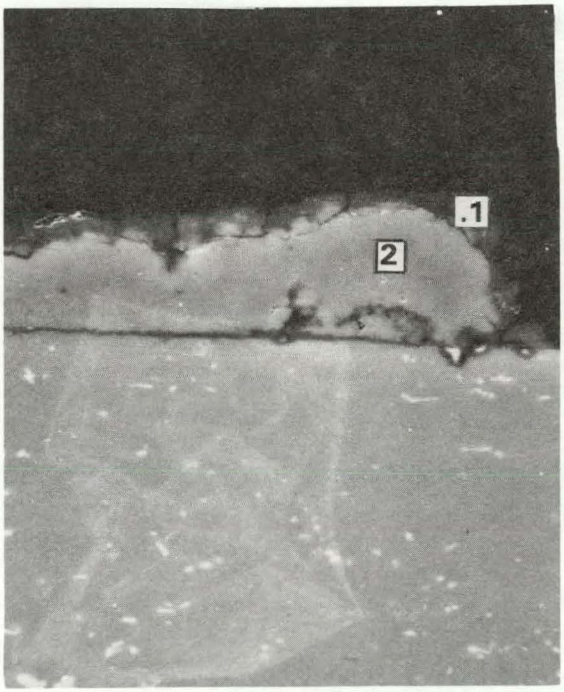


1000x*(#B-15, 617)

SEM microprobe analyses, at the two points indicated, normalized to aluminum

	Si/Al	Ca/Al	Cl/Al	
pt 1	0.42	0.15	--	
pt 2	0.05	0.04	0.02	
	S/Al	Fe/Al	K/Al	Zn/Al
pt 1	0.12	0.01	0.06	--
pt 2	0.01	0.03	--	0.03

Figure 3-13. Interior Pit Morphology of a Large Pit on Unanodized Aluminum Plate After 1000 Cycles (32 Days) at 2X Concentration Factor and 60^{o}C Specimen Temperature



1000x*(#B-15, 621)

SEM microprobe analyses, at the two points indicated, normalized to aluminum

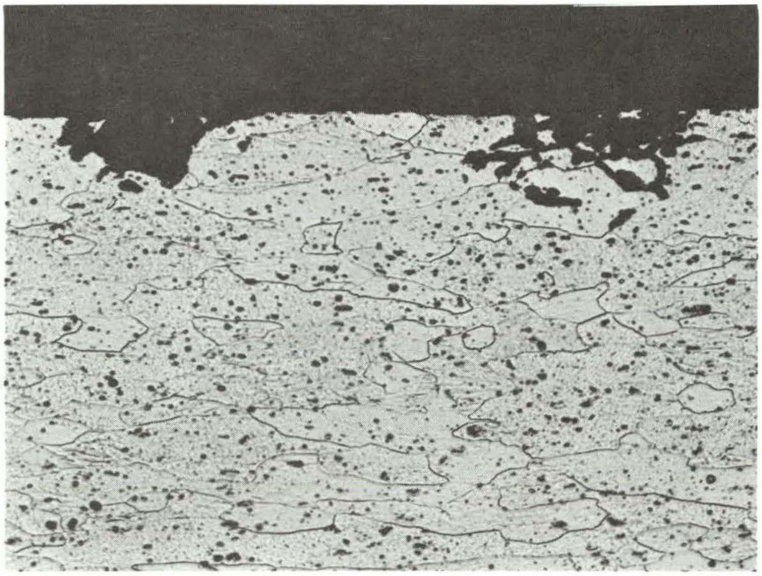
	Si/Al	Ca/Al	Cl/Al	Na/Al
pt 1	0.77	0.48	0.10	0.07
	S/Al	K/Al	Zn/Al	Cu/Al
pt 1	0.11	0.33	0.01	0.01
pt 2	Ca with barely detectable amounts of Al, Si, P & S.			

Figure 3-14. Plate Section Micrograph Through a Deposition Ribbon

*Please note that the illustrations on this page have been reduced 10% in printing.

350x*(#4N 1449C)

a) Micrograph of a typical pit



350x*(#4N 1449D)

b) Etched view of same area as shown above; Etched in HF for 10 sec

Figure 3-15. A Cross-Section of the Plate Shown in Figure 3-12 (at 2X for 1000 Cycles): Etching Reveals Intergranular Attack

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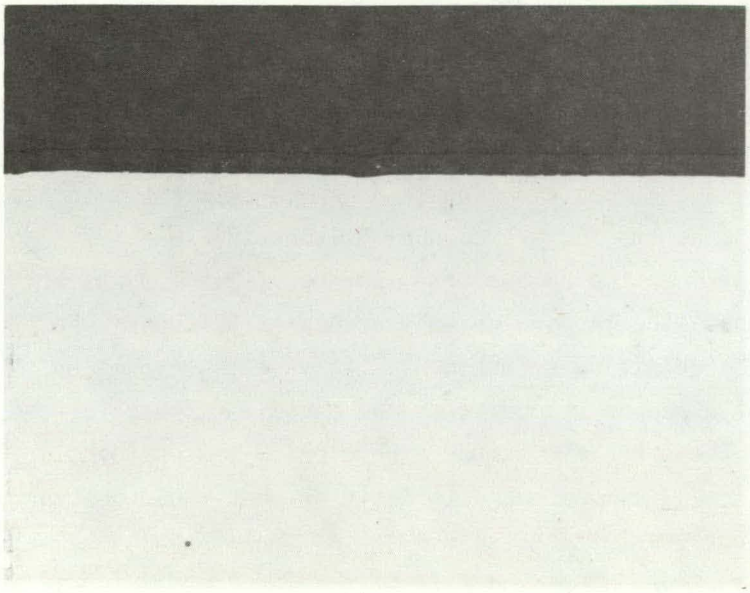
*Please note that the illustrations on this page have been reduced 10% in printing.



200x*(#4N 1356B)

Figure 3-16. Anodized Aluminum Alloy 1100 Plate

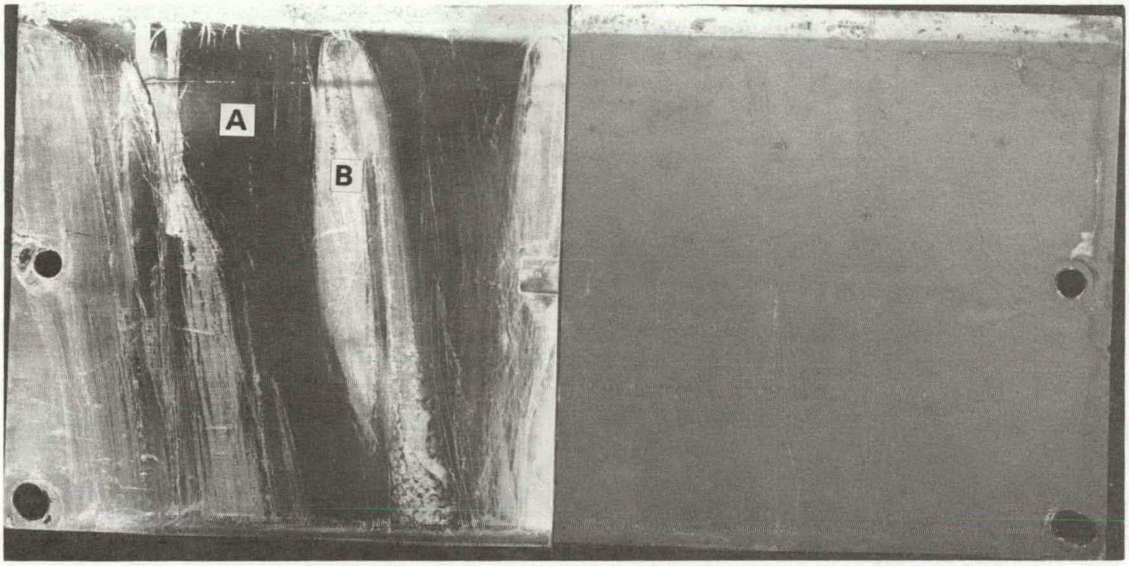


Figure 3-17. A pictorial comparison of the differences that anodizing aluminum has on corrosion resistance. (Both plates were subjected to the same conditions. The right plate was anodized, the left plate was not.) Dark areas (A) are thin film corrosion and light areas (B) are deposition ribbons.

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*Please note that the illustrations on this page have been reduced 10% in printing.

3.3 CHARACTERISTICS OF DEPOSITION

Deposition on the HOTERV core increased as the substrate temperature increased. The higher temperature associated with the heated tubes (compared to the fins and unheated tubes) not only encouraged deposition in the tube vicinity but also had some effect on the composition, as the SEM microprobe analyses in Figure 3-6 show. Note the sudden increase in Ca/Al on the hottest fin surface. This fin was at 60°C when deluged. This is above the threshold temperatures of 57°C observed by Knudsen and Story (17) at which calcite was formed by steady-state deposition. This type of deposition is not expected according to the Langelier Index for the deluge water in those tests. The other fin surfaces were below this threshold temperature and the deposit formed is more characteristic of what would be expected if the deposit resulted from the total dissolved solids contained in the wetting film.

The solubility of some scale-forming salts (such as $CaCO_3$) decreases with rising temperature. Additionally, water films adjacent to heated surfaces tend to become more concentrated than the bulk water, and solubility of scale-forming salts is locally exceeded. These mechanisms result in scale formation. This contributes to the observed deposition being heaviest on the hotter tube surfaces. About two-thirds of the precipitate formed on the HOTERV core could not be removed by deionized water rinsing after each run. The anodized plate was uniformly 60°C and the HOTERV core temperature averaged about 48°C; this measured temperature variation between the core and plate as well as on the core itself affected the distribution and amount of deposition which formed on the core. The temperature dependence of this mechanism may account for the higher weight gain per unit area observed on the anodized plate specimens.

The deposit on the plate is rich in calcium, shown by the SEM microprobe analyses (Figures 3-12 and 3-14). From the measurements of specimen temperature and from comparing these deposits to those observed on the HOTERV core, it was concluded that the plate deposits were affected by the higher plate temperature. This increase would principally consist of a larger steady state retrograde solubility-type deposition that resists redissolution.

3.4 CHARACTERISTICS OF CORROSION

The corrosion found on the HOTERV core was suspected to be strongly associated with breaks or pores in the anodized layer. Frequently it was observed that an Fe-Si rich area in the aluminum matrix (typical of 1100 aluminum alloy) was associated with observed pits, particularly with the more developed ones. The tests that were conducted were not long enough to permit formulating conclusions concerning pit growth and core lifetime.

The corrosion observed on the plate was present as a thin film mixed with the deposition "ribbons." These corrosion films frequently displayed the "interference color" effects observed for other thin film metal oxides. The pits observed in Figures 3-12, 3-13 and 3-15 were about 50 m deep, maximum. SEM microprobe analyses of several pits and surrounding areas were conducted to determine whether species which contributed to the pitting were discernible (Figures 3-12, 3-13).

Chloride was observed by this method in all pits we studied. A possible mechanism is the formation of corrosion cells under deposits and/or in anodized layer pores, particularly those which penetrate the anodized layer completely.

The principal corrosion effect of the DIW rinse was noted on the unanodized plate specimens. The thin film corrosion layer appeared to be thinner on the rinsed specimens than on the unrinsed specimens.

Anodization of plate specimens eliminated the thin film corrosion and pits on the two samples tested. No difference could be found between the two methods of sealing (K_2CrO_2 and boiling water) of the anodized films because there was no visible corrosion on either sample.

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Section 4

STEADY-STATE DEPOSITION - CDL MOD-2

Deposition (scaling) on heated surfaces forms primarily by two phenomena: 1) nucleation, precipitation and growth of an adherent layer of insoluble salt from a saturated solution under continuous wetting (21) and 2) deposition of crystals of dissolved solids by solvent evaporation. In a wet/dry system both mechanisms are possible but the relative contributions of each mechanism to overall scale buildup is uncertain. Steady-state scale (Mechanism 1) formed from inverse solubility salts such as calcium carbonate, is tightly adherent to the heated surface and is difficult to remove. Deposition from dissolved solids in film drying (Mechanism 2), however, is loosely held and appears to be controllable by a soft water wash. Return to solution and mechanical removal of film drying deposit will depend upon rinse water quality, duration of rinse, and rinse water velocity. These parameters will be determined by further experimentation.

Initial deposition studies in CDL (to run #7) using the HOTERV heat transfer surface employed a cyclic (alternating wet-dry) operating mode with small ion inventory. These runs showed modest scaling. Recent system modification, however, has substantially increased the available supply of precipitating ions with resulting increase in scaling from continuous (steady-state) deluging. This section (4) examines some of the factors which contribute to and control steady-state deposition.

4.1 CONSTANT ION INVENTORY

Precipitation of slightly soluble electrolyte from solution is dependent upon local concentration, temperature and solubility product constants (Ksp) for the particular salts possible from available ion combinations. Precipitate crystals agglomerate into scale on hot surfaces. Precipitation will continue as long as local ion combinations exceed the Ksp for the specific salt. Control of precipitate is usually done by: 1) removal of hardness (Ca^{++}, Mg^{++}) by ion exchange, 2) use of anti-nucleating agents to prevent crystal growth, or 3) lowering concentration by blowdown.

In a large system subjected to continuous solute concentration from solvent evaporation, scale-forming ions (particularly Ca^{++}, CO_3 , and HCO_3) must be controlled to minimize scale accumulation on heat transfer surfaces. The ACT cooling system has a deluge volume to cooling surface area of approximately 0.4 gal/ft^2. Mod-1, using the HOTERV core, has a deluge volume to cooling surface area of about 0.14 gal/ft^2. In order to provide a more stable supply of scale forming ions as experienced in a full-scale cooling tower, CDL deluge volume was increased ten-fold to 106 ℓ. This change provided a CDL deluge volume to cooling surface area of 0.8 gal/ft^2. Table 4-1 presents CDL data for runs after installation of the large deluge reservoir. Run #7 at 4X concentration differed from previous runs in that the CDL core was continuously wet for 135 hr (equivalent total wet time in previous cyclic runs) with one drying at the conclusion. Core weight gain after this steady-state exposure was 5.3 g, a factor of two greater than a 4X cyclic run with equivalent wet time but with the original Mod-1 water volume. Deionized water is automatically added to all runs to replace evaporation. Concentration changes in Ca^{++}, alkalinity, and conductivity suggest that most scaling occurred during the first 72 hr of deluge.

Two important observations can be noted from run #7. Stabilizing the supply of inverse solubility ion species (larger water reservoir) will logically enhance opportunity for precipitation at hot surfaces where local Ksp values are exceeded. This scaling on and near hot tube surfaces occurs from water whose Langelier (saturation) index from the bulk water predicts minimal scaling, an expected result when localized solubility limits are exceeded in regions of high heat flux.

The result of maintaining ionic concentrations in excess of solubility limits at hot spots is demonstrated in run #10. Delugate was held at or near the 4X level during a 128 hr steady-state run by continuously adding a slow 4X water drip to the reservoir maintaining a high supply of ion species. During the 128 hr run approximately 175 ℓ of drip were added to the system. Evaporation loss held water levels within reservoir limits. Core weight gain under these conditions was 12.5 gm. Considering $CaCO_3$ to be the primary scale, a mass balance of all Ca^{++} ions present during the run was taken. The resultant calculation shows in theory a possible 13.2 g scale as $CaCO_3$. The agreement with actual deposition is close. The Ca^{++}, CO_3 , and HCO_3 ion concentrations and the solution pH for run #10 produce a Langlier Index of +0.13, a value not normally indicative of precipitation. This illustrates scale buildup which can occur in untreated water when calcium and bicarbonate ions combine in regions of high heat flux (hot tubes). Figure 4-1 shows visible scale buildup on tips of cooling fins and heated tube surfaces after exposure to 4X deluge in run #10.

Table 4-1

WATER CHEMISTRY AND RESULTING DEPOSITION

Run Number	7	7	7	7	7	10	10	10	10	10
Date	11-10-78	11-13-78	11-14-78	11-15-78	11-16-78	1-2-79	1-3-79	1-4-79	1-5-79	1-8-79
Concentration Factor (Theory)	4	4	4	4	4	4	4	4	4	4
Running Time (Hours)	0	72	96	120	135	0	24	48	72	128
Sample Temp (^{o}C)/ Deluge Temp (^{o}C)	47/35	47/35	47/35	47/35	47/35	37	40	41	38	40
pH	8.5	8.3	9.2	8.1	8.0	8.4	8.6	8.5	8.5	8.4
Conductivity (μmho/cm)	390	220	245	225	219	820	770	485	540	400
Alkalinity -CO_3(mg/ℓ)	5.8	0	0	0	0	0	0	0	0	0
-HCO_3(mg/ℓ)	55.3	27.6	24.7	26.1	26.9	152	102	55	66	49
TDS (mg/ℓ)	--	--	--	--	--	512	443	268	320	271
SiO_2 (mg/ℓ)	32	11	10	80	80	64	52	32	35	22
SO_4(mg/ℓ)	90	48	44	43	42	190	160	120	130	120
Al (mg/ℓ)	0	0.06	.12	.19	0.22	0	0	0	0.01	0.07
Ca (mg/ℓ)	11.5	7.0	6.34	5.83	5.31	22	18	12	12	10
Mg (mg/ℓ)	1.22	.59	.53	.54	0.52	2.5	2.1	1.2	1.4	1.4
Fe (mg/ℓ)	.053	.032	.026	.027	.029	.63	.02	.01	.01	.01
Na (mg/ℓ)	70.6	37.1	35.2	33.7	32.7	129	112	66	76	67
Cl (mg/ℓ)	20.6	11.9	11.0	10.3	10.3	38	34	19	24	22
Langelier Index	+0.06	--	-0.94	--	-1.22	+0.7	--	--	--	-.05
Ryznar Index	8.38	--	10	--	10.4	7.0	--	--	--	9.4
Weight Gain	--	--	--	--	5.3	--	--	--	--	12.5

--Not measured.

Table 4-1

(contd)

Run Number	14	14	14	14	15	15	15	15
Date	8-28-79	8-29-79	8-30-79	9- 1-79	9- 6-79	9-7-79	9-10-79	9-11-79
Concentration Factor (Theory)	2	2	2	2	4	4	4	4
Running Time (Hours)	24	48	72	125	0	28	96	120
Sample Temp (^{o}C/ Deluge Temp (^{o}C)	50/43	50/38	50/41	50/41	52/40	52/40	52/40	52/40
pH	8.2	8.2	7.9	7.5	7.5	7.4	7.5	7.4
Conductivity (μmho/cm	--	--	--	--	--	--	--	--
- CO_3(mg/ℓ)	0	0	0	0	0	0	0	0
Alkalinity - HCO_3(mg/ℓ)	51.3	16.8	17.7	12.4	71.3	--	77.4	60.6
TDS (mg/ℓ)	303	311	345	372	474	--	520	418
SiO_2 (mg/ℓ)	--	--	--	--	--	--	--	--
SO_4 (mg/ℓ)	--	--	--	--	--	--	--	--
Al (mg/ℓ)	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.3	0.3
Ca (mg/ℓ)	12.8	14.2	13.7	13.8	4.6	12.6	19.3	18.7
Mg (mg/ℓ)	1.3	1.4	1.5	1.6	2.1	1.7	2.2	2.4
Fe (mg/ℓ)	<0.1	<0.1	<0.1	<0.8	--	--	--	--
Na (mg/ℓ)	71	70	66	64	143	142	121	111
Cl (mg/ℓ)	--	--	--	--	--	--	--	--
Langelier Index	+0.08	--	--	-1.51	-1.4	--	-1.0	--
Ryznar Index	8.3	--	--	10.2	10.3	--	9.5	--
Weight gain (gm)	--	--	--	-2.3	--	--	--	8.1

--Not measured.

Table 4-1

(contd)

Run Number	16	16	16	16	16	16	17	17	17	17
Date	9-20-79	9-21-79	9-23-79	9-24-79	9-25-79	9-26-79	10-24-79	10-24-79	10-25-79	10-28-79
Concentration Factor (Theory)	4	4	4	4	4	4	4	4	4	4
Running Time (Hours)	0	24	72	96	110	124	24	30	56	138
Sample Temp (^{o}C/ Deluge Temp (^{o}C)	52/38	52/38	52/38	52/38	52/38	52/38	51/38	51/38	51/38	51/38
pH	8.2	7.0	6.9	4.4	4.4	4.4	7.9	7.2	7.2	7.7
Conductivity (μmho/cm)	765	720	410	530	1120	390	150	61.6	320	184
- CO_3(mg/ℓ)	0	0	0	0	0	0	--	--	--	--
Alkalinity	132	73.7	34	0	0	0	29.6	56	14.5	13.3
- HCO_3(mg/ℓ)										
TDS (mg/ℓ)	582	439	311	425	972	287	109	449	240	104
SiO_2 (mg/ℓ)	--	--	--	--	--	--	--	--	--	--
SO_4 (mg/ℓ)	19.6	214	142	107	143	43.7	30.8	192	96	42
Al (mg/ℓ)	<0.1	0.2	0.4	1.0	24	4.7	1.2	0.13	0.16	0.23
Ca (mg/ℓ)	26.8	19.1	17.4	19.3	4.4	2.2	8.0	21.4	10.5	5.4
Mg (mg/ℓ)	2.8	2.1	1.5	2.1	0.4	0.3	0.6	2.1	1.2	0.77
Fe (mg/ℓ)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Na (mg/ℓ)	161	119	84	105	254	82	23.3	105	54.2	26
Cl (mg/ℓ)	34.1	24.9	24	29.5	5.3	1.7	7.1	34.3	15.4	6.2
Langelier Index	0.66	--	--	-0.6	--	--	-0.75	--	--	-1.4
Ryznar Index	6.88	--	--	5.6	--	--	9.4	--	--	10.6
Weight gain (gm)	--	--	--	--	--	4.7	--	--	--	5.3

--Not measured.

Table 4-1

(contd)

Run Number	18	18	18	18	18
Date	11-14-79	11-15-79	11-16-79	11-19-79	11-20-79
Concentration Factor (Theory)	5	5	5	5	5
Running Time (Hours)	20	45	67	139	173
Sample Temp (^{o}C/Deluge Temp (^{o}C)	51/37	51/37	51/37	51/37	51/37
pH	7.2	7.5	7.3	7.2	7.5
Conductivity (μmho/cm	828	978	918	1056	835
- CO$_3$(mg/ℓ)	--	--	--	--	--
Alkalinity					
- HCO$_3$(mg/ℓ)	12	33	9.8	29	15
TDS (mg/ℓ)	573	747	503	788	756
SiO$_2$ (mg/ℓ)	--	--	--	--	--
SO$_4$ (mg/ℓ)	295	383	253	222	219
Al (mg/ℓ)	0.19	0.18	0.7	0.6	0.29
Ca (mg/ℓ)	26	28	20	23.7	22.7
Mg (mg/ℓ)	3	3	2.2	2.6	2.7
Fe (mg/ℓ)	<0.1	<0.1	<0.1	<0.1	<0.1
Na (mg/ℓ)	142	187	147	205	182
Cl (mg/ℓ)	38	42	28.5	33.7	33
Langelier Index	-1.4	--	--	--	-1.0
Ryznar Index	10	--	--	--	9.6
Weight gain (gm)	--	--	--	--	8.0

--Not measured.

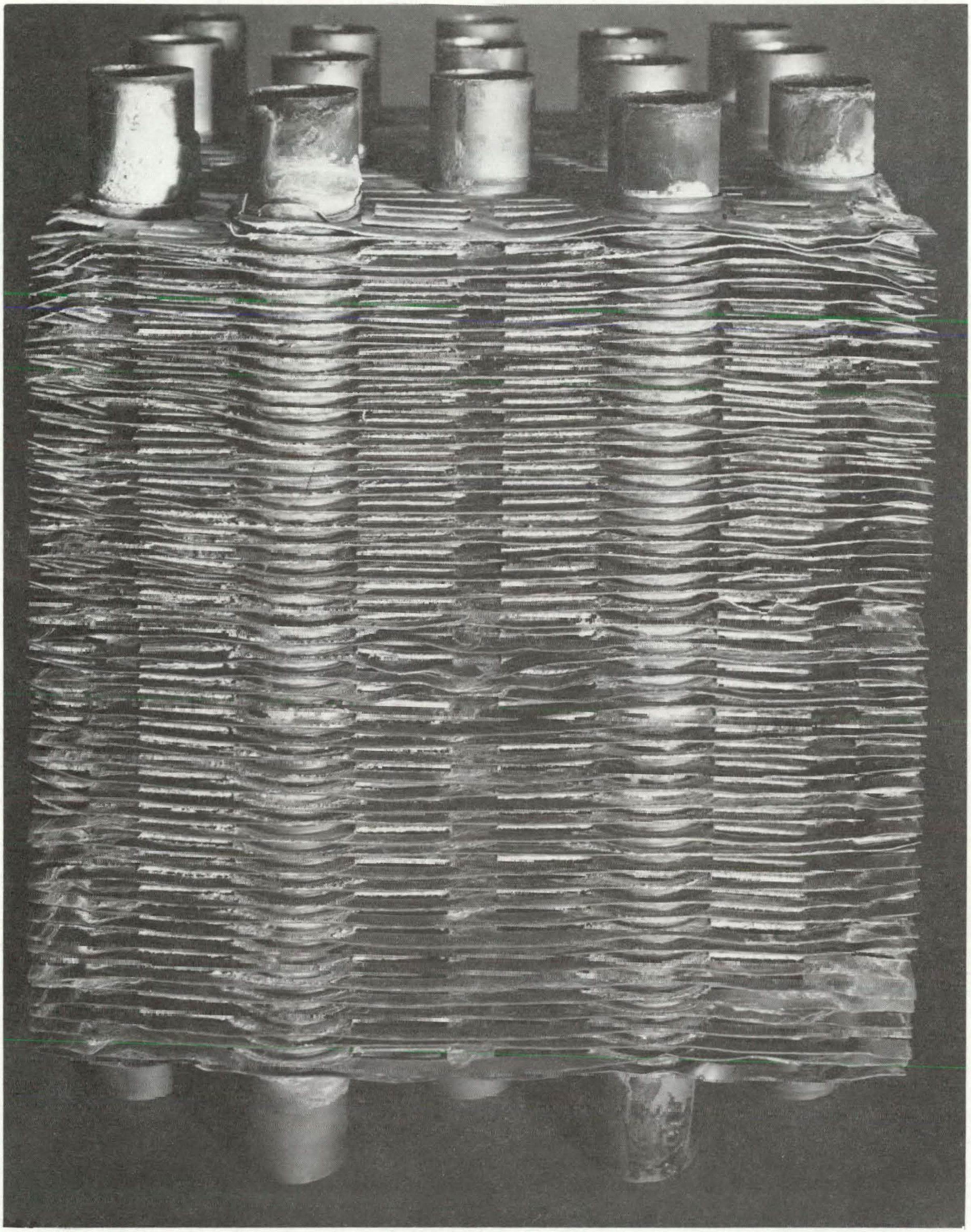

Figure 4-1. Deposition on HOTERV Surface After CDL Run #10 at 4X Concentration

4.2 LOCALIZED HOT-SPOT DEPOSITION

Two thirds of the HOTERV core tubes in the CDL Mod-1 system were heated by high energy density heating elements. Thermocouples placed in unheated core tubes show core temperatures of 49^{o}C when wet and 72^{o}C when dry. Liquid-tube interfaces are in excess of 54^{o}C when being deluged, a temperature level promoting deposition of inverse solubility salts. Heated tubes (H) seen in Figure 4-2 have heavy scale compared to unheated tubes containing thermocouples (TC) in the HOTERV core after 254 wet/dry cycles in 4X water. Concentration was maintained at 4X by addition of a constant drip. It is visibly evident that scaling is primarily confined to the high heat flux surfaces with virtually no scale on the unheated TC tubes. This highly concentrated scaling is not representative of deposition which will occur on ACT HX surfaces with tubes uniformly heated by 52^{o}C ammonia at inlet. Changes in method of core heating and techniques of deluge dispersion, described in Section 2.1.1, improved core temperature distribution and core wetting. These changes were in effect with run #14.

4.3 DEVELOPMENT OF ACT OPERATING CRITERIA

As the construction and operation of ACT Facility approaches, current and future deposition and corrosion studies will be focused on the relative importance of deluge chemistry, rinse cycle, pH control, in situ core cleaning techniques, and water treatment to ACT operation. Of paramount concern will be the influence of various scale-controlling procedures on long-term aluminum corrosion. From these studies will come recommendations for deluge control and operation to improve ACT service life. This philosophy prompted the above described CDL modifications, adding flexibility to loop operation and providing testing conditions closer to expected tower operating parameters.

4.3.1 Post-Modification CDL Results

Loop runs #14 through #18 were conducted in the modified system using the HOTERV surface. Runs beyond #18, to be discussed in a subsequent report, will employ a model Trane Co. heat exchanger, prototypic of the wet/dry heat transfer surface to be used at ACT.

4.3.1.1 Concentration Effects

The initial run with improved core heating (#14) was done at 2X concentration with pH 7.5. The HOTERV core was exposed to 125 hr of continuous deluge at 52^{o}C uniform core temperature and 38^{o}C deluge temperature. Air flow across core fins

Figure 4-2. Arrangement of Heated (H) Tubes and Cool Thermocouple (TC) Tubes in HOTERV Core Tested in CDL

was controlled at 91.4 to 121.9 cm/sec causing evaporation loss under system conditions of approximately 3.78 /hr, replaced automatically by deionized water.

Core weight loss for run #14 was 2.3 gm (13.5 mg/dm^2), probably due to dissolution of old surface scale or dissolution of aluminum. The aluminum ion concentration in the delugate, however, did not increase during the run. Weight loss must therefore be attributed to old scale removal (principally Mg, Ca) rather than Al dissolution. By visible inspection the core showed no evidence of any scale formation or crystalline deposition from the steady-state exposure at 2X.

Run #15 duplicated run #14 except concentration was increased to 4X. Core weight gain after 125 deluged hours at this higher concentration was 8.1 gm (47 mg/dm^2) contrasted with weight loss at the lower concentration. Unlike the apparently clean core after run #14, the leeward core face following run #15 had substantially visible, loosely adherent deposition. The localized accumulation of deposit might be due to water entrainment in the air stream with resultant localized concentration increase on the leeward face. Another possible reason could be the channeling of delugate flow in the distribution system.

4.3.1.2 Cyclic Operation

The marked reduction in core weight gain by use of 2 to 3 ppm phosphate additions to cooling water (22) and a deionized water rinse between alternating wet/dry cycles is seen in run #16 at 4X concentration. A 4 ppm polyphosphate water conditioner was added to the delugate as recommended by Hatch and Rice (22). Cooling water was cycled one hr and 45 min followed by 13 min drying. Immediately following cessation of deluge a two min deionized water rinse wetted the core surface to remove delugate water films. Total wet time for run #16 was 124 hr (70 wet/dry cycles), a time equivalent to run #15. Core weight gain for the rinsed and water-conditioned exposure was 4.7 g compared to 8.1 g of run #15. Part of this weight difference may have been due to CDL operation for two days with delugate pH in the 4 to 5 range. At this low pH the bicarbonate ion was totally removed and aluminum ion concentration increased sharply (10 ppm) in the delugate. This run demonstrated the combined action of Ca^{++} complexing with polyphosphates, film rinsing, and low pH on scale prevention. A pH of 4 to 5, however, is not recommended as it obviously is corrosive to aluminum.

Since steady-state deposition is a major (perhaps the primary) contributor to scale buildup, the length of wet cycle in run #17 was increased to 5 hr, 45 min. A two min deionized water rinse immediately followed deluging. A 13 min. drying period completed the cycle as in previous runs. Threshold treatment and close control of pH (7.0 to 7.3) stabilized the 4X concentration delugate to match run #16. Total wet time for run #17 was 138 hours. A slight increase of 0.6 gm in core weight gain in #17 over that observed in #16 can be attributed to the longer wet cycle and the additional 14 hr greater exposure length. Lack of visible scaling resulting from run #17 is evidenced in comparing Figure 4-3a,b.

The effect of increasing concentration is readily observed in run #18 where delugate is held between 5X and 6X with scaling weight gain increasing to 8.0 gm (50% > run #17). Longer (173 hr) exposure time accounts for part of the #18 weight increase, but greater delugate concentration is a strong factor in the amount of deposition with time. Uniform core temperature again results in even distribution of scale. If we allow 6 hr/d deluge for 6 mo/yr, the 8.0 gm weight gain roughly approximates a 1.8 mil thick uniform scale buildup in three years operation. The 5X concentration exceeds recommended limits.

4.3.1.3 Alclad Aluminum - Kern Water Interaction

The Trane Co. has been selected to supply wet/dry heat exchangers for the ACT Facility. The proposed TRANE wet/dry HX will have the following aluminum alloy composition: tubes - Alclad (3003 base-7072 clad), fins - 7072. Since the model TRANE core to be used for scaling studies is constructed of 3003 alloy, core corrosion resistance must be measured on representative materials samples independent of the scaling investigation.

Two Alclad (3003 base-7072 clad) plates 15 cm x 30 cm x 0.15 cm thick were electrically heated and deluged concurrently with the HOTERV core in runs #14 and #15 through #18. Monitored plate temperatures were generally 38 to 43°C in the center and 44 to 49°C on ends.

After 125 hrs continuous deluge at 2X concentration, plate #1 (Figure 4-4) gained 0.1 g. Small isolated surface spots of attack are evidenced on the 7072 clad. These surface pits, however, extend no deeper than the clad 7072 and appear to be spreading laterally rather than penetrating deeper. The clad is providing cathodic protection to the base metal, as design theory predicts, and attack is confined to the cladding.

Plate #2 was exposed to 4X deluge during four sequential CDL runs (#15, #16, #17, #18) for a total of 555 wet hrs. Figure 4-5 shows many localized areas of attack over the entire plate surface. Individual spots are growing laterally with length

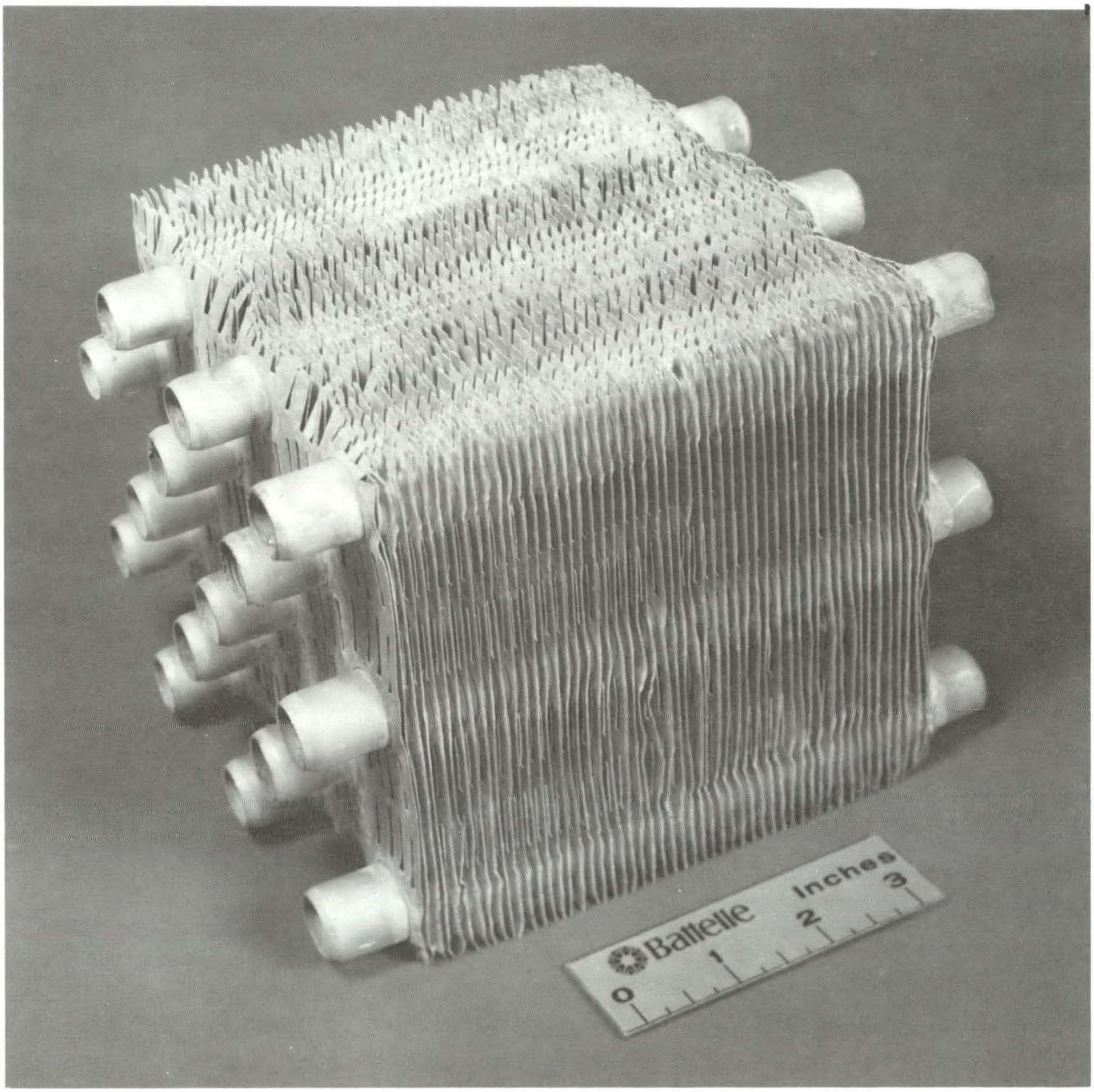

Figure 4-3a. HOTERV Surface Before Run #17

of exposure, but corrosion is confined to the cladding. A metallographic section through a surface pitted area (Figure 4-6) shows typical pitting dimensions. Alclad coating appears to also afford substantial electrochemical protection to the base metal at cut edges and scratches. This may be important in heat exchanger assembly.

A question remains as to length of exposure time required for isolated corrosion spots to bridge, indicating final consumption of the protective coat. Total tube

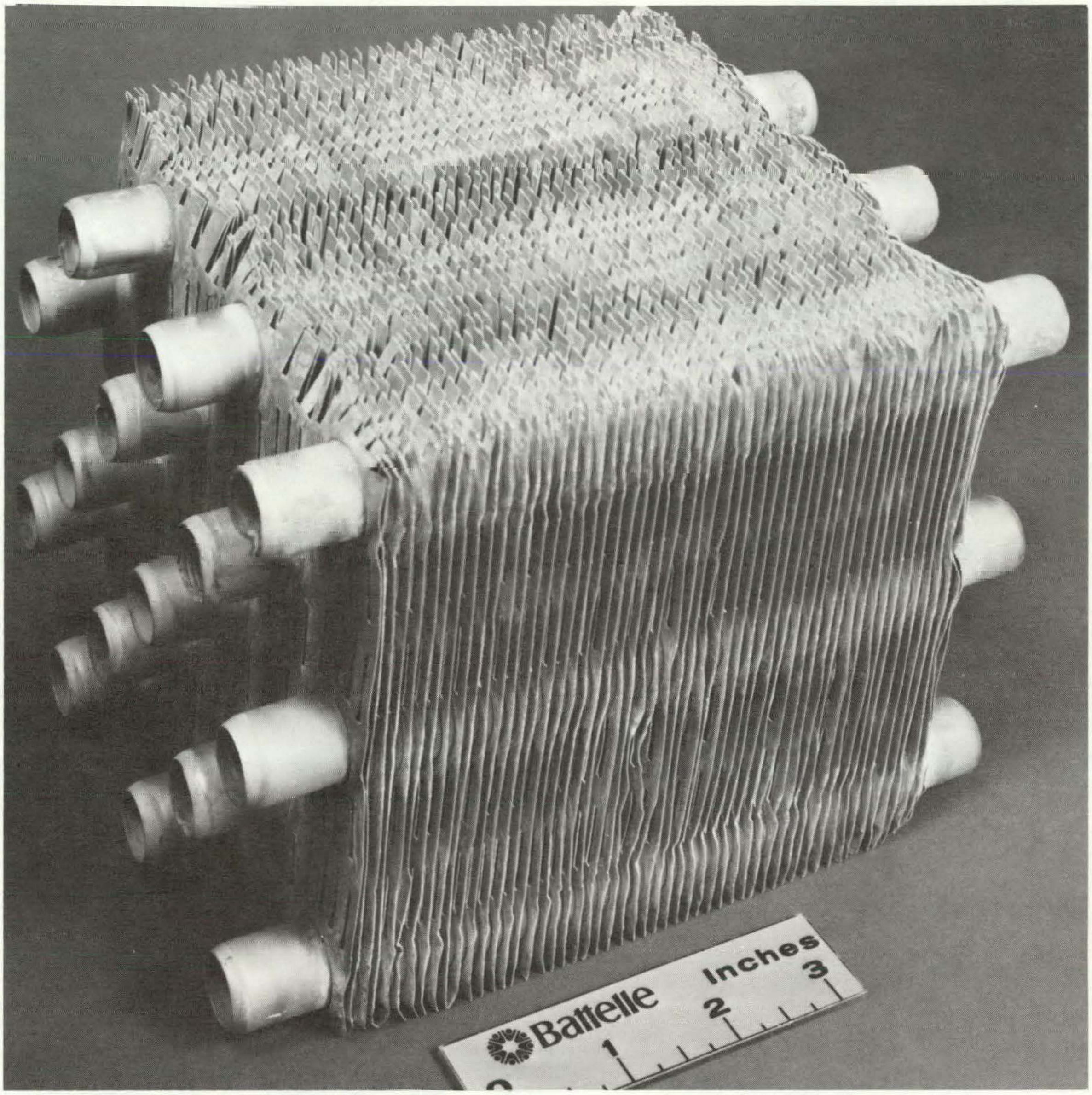

Figure 4-3b. HOTERV Surface After Run #17

life will then be the sum of the rate of 7072 cladding consumption and the rate of 3003 pitting penetration through the wall. A long-term exposure of several aluminum alloys (including 3003) with various protective coatings (Alclad, anodized, etc.,) to simulated Kern water is in progress and will help formulate estimates of material life in deluged aluminum heat exchangers.

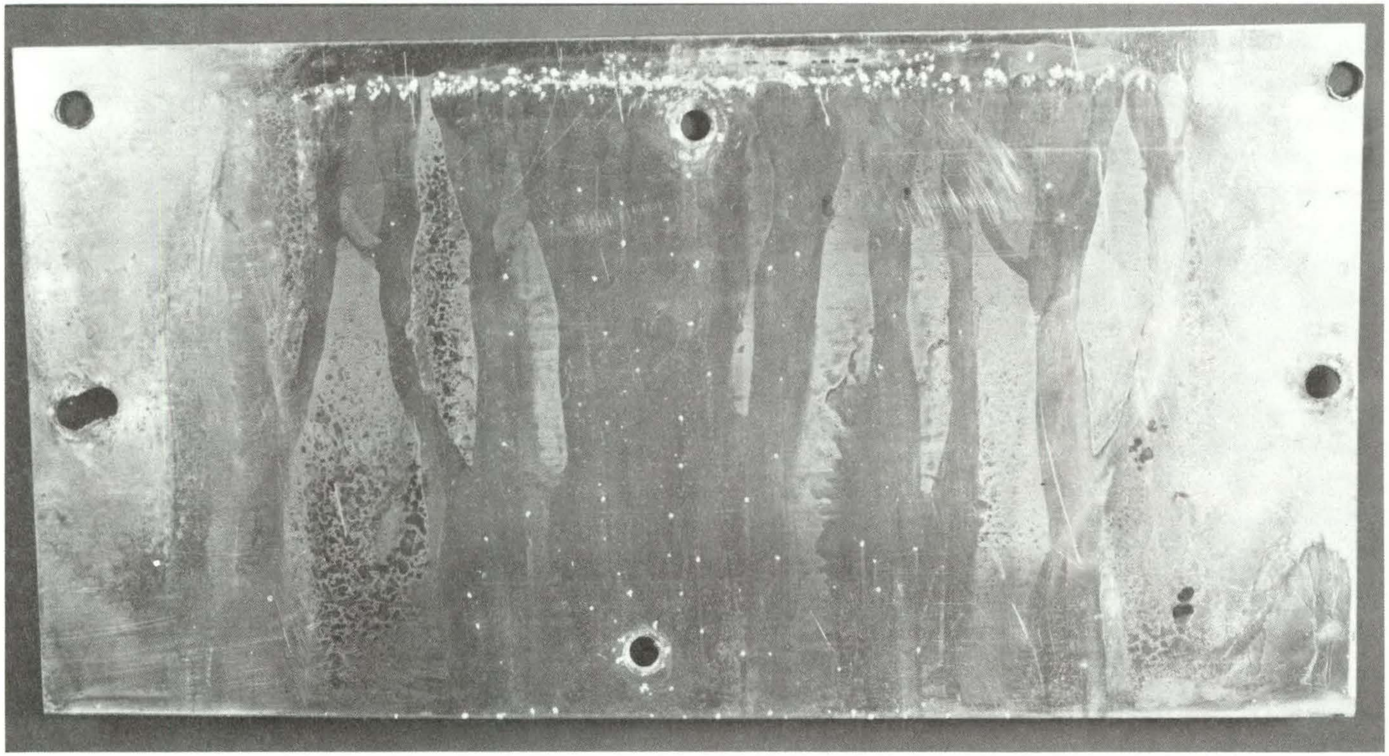

Figure 4-4. Alclad surface after 125 hr exposure to 2X deluge. Note isolated reaction spots, few in number.

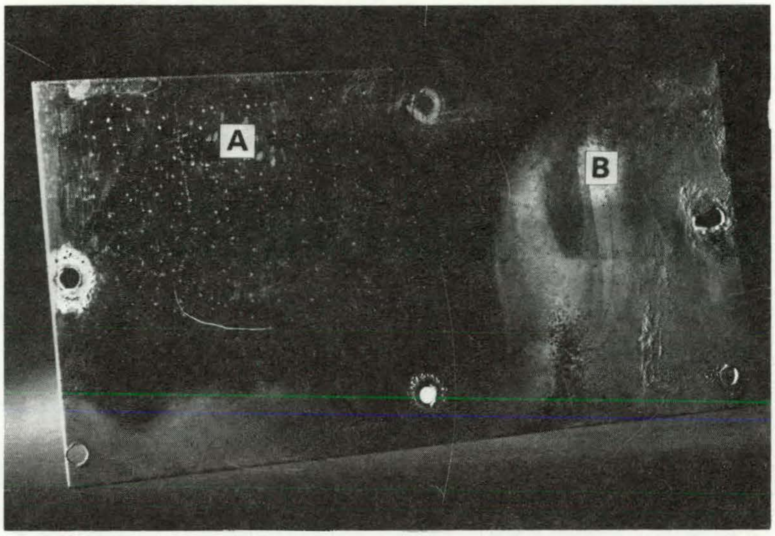

Figure 4-5. Alclad surface deluged 555 hr at 4X concentrations. Note large increase in number of reaction areas (A). White deposit (B) is primarily splash evaporation.

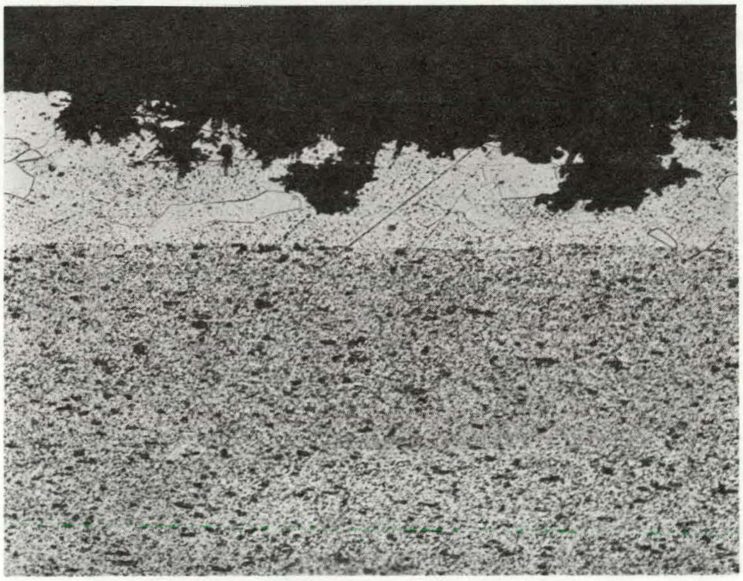

Figure 4-6. Alclad Plate Section Through Typical Reaction Area Showing Pit Confined to Surface Clad

Section 5

APPLICATION TO FULL-SCALE SYSTEMS

CDL corrosion/deposition studies of air and deluge-cooled aluminum alloy surfaces provide needed information for specifying ACT facility cooling water chemistry and system operation. Results to date have shown the following:

- Two types of scaling mechanism are generally recognized, precipitation of low solubility salts in heated solution and deposition of dissolved solids from evaporating solvent films. The first (steady-state) mechanism is controlled by attention to water chemistry, pH, water treatment, and good heat transfer design. The second is minimized by reducing dissolved solids, removal of delugate film by soft water rinsing, and uniform core wetting. A sodium zeolite softener treats the water to less than 5 ppm calcium as $CaCO_3$.

- Scale buildup on heat exchanger surfaces appears to be approximately linear with water impurity concentration and time of exposure to delugate. The amount of scaling occurring on a given area will depend on the local temperature and concentration of low solubility impurity species at that specific area. Considering these variables in ACT operation, a maximum of four cycles of concentration may be reasonable as operating procedure but future work on the TRANE core may revise this limit slightly downward.

- As a corollary to the above, scale buildup during steady-state operation is heaviest at hot spots on the heat transfer surface. Cooling tower design that minimizes hot spots is important in controlling scaling.

- Holding pH at neutral values (7 to 7.5) is essential to scale control. Acidic solutions tend to be corrosive to aluminum, while basic solutions promote increases in the bicarbonate ion with resultant calcium reaction.

- Langelier and Ryzner indices are generally useful in steady-state operation for predicting scaling tendencies of a given solution chemistry and temperature. Some scaling, however, does occur from solutions with neutral indicies. In cyclic operation, deposition of dissolved solids occurs as delugate film evaporates. Films are produced by incomplete wetting (splashing) or cessation of deluge flow. These films may be capable of removal by a short (2 to 3 min.) rinse with soft water removing the residual delugate film. Experimentation continues to determine how effective the rinse will be in reducing scale accumulation.

- Exposing aluminum samples to CDL delugate indicates that the well water to be used at the ACT facility could be sufficiently aggressive to cause pitting corrosion on fin surfaces or edges, or crevice corrosion at fin-tube junction. Some form of metal surface protection such as anodizing, cladding, and close pH control would be cost-effective in extending cooling tower life. Additionally, a continuous corrosion monitoring system of representative heat exchanger materials is recommended during ACT operation.

- Preliminary indications suggest that addition of a few ppm of anti-nucleating agents to the delugate and employment of a soft water rinse following the deluge cycle will substantially reduce buildup on the wet/dry ACT cooling tower. An analysis is being conducted to determine the economics of water treatment to allow operation at higher cycles of concentration

Deposition studies provide a preliminary basis for extrapolation of deposition effects on fin-tube type heat exchanger performance at plant lifetimes (40 yrs) under deluged dry-cooling conditions. Based on CDL Mod-1 results, estimated scale buildup, if uniform, would amount to 40 μm over that time frame, for a HOTERV surface, using simulated Kern water at a 4X concentration factor. This does not significantly reduce the overall heat transfer even for the unrinsed sample.

As described in Section 4.0, increasing the volume of CDL cooling water (Mod-2) stabilized concentration of low solubility dissolved solids. This was reflected in an increase in scaling for Mod-2 runs at exposure times equivalent to Mod-1. Using the model TRANE core exposed at 2X concentration, a weight gain of 7.5 mg/dm^2 was measured after 130 hr. Estimating a 6/hr/d deluge operation for 6 months, this projects to 10.6 μm scale buildup in three years. This is conservative, for some of the weight gain on this initial TRANE core exposure was due to oxidation of aluminum core tube inside surfaces exposed to core heating water. Deposition, however, was not uniform but occurred most heavily in certain areas where deluge flow was uneven or where splashing was evidenced.

There are other alternate solutions to removing or preventing scale formation on heat exchanger surfaces. Los Alamos scientific laboratory greatly improved a bad scaling problem on steel and copper cooling surfaces by use of chemical additives to make-up water (<u>18</u>). Initially, the treatment consisted of a mixture of EDTA type chelants and two corrosion inhibitors. A word points out that excessive concentrations of EDTA can be very corrosive. Currently, a composition consisting of phosphonates, low molecular weight polyacrylates, and two corrosion inhibitors at 20 ppm in make-up water is being used. The tenacious, high silica scale that once completely blocked water and air flow passages in the Los Alamos water-cooled heat transfer units appears to be effectively controlled. Use of chemical additives to make-up water for scale control at ACT facility needs further investigation. Corrosion inhibitors may not be justified in an aluminum alclad system.

It may be that in certain applications the deposition problems do not justify the cost of chemical additives for scale control. Deposits could be chemically removed as needed at times when sections of the dry-cooling unit could be taken out of service without degrading plant operation. The choice between control or periodic removal would depend on relative costs and performance including projected service life.

Careful materials selection will also tend to reduce corrosion problems. Using copper alloys for deluge piping with aluminum heat exchangers almost guarantees a maintenance problem. Similarly, allowing the deluge water to come in contact with concrete or iron piping will cause additional deposition problems, irrespective of the heat exchanger material. Wind-borne materials can also adversely affect heat exchanger performance. This requires careful site selection for the deluged units to minimize effects of air-borne debris. Both particulates and vapors could jeopardize the aluminum heat exchanger corrosion resistance.

Biofouling is a potential problem. On surfaces wetted and dried, biofouling may not be a problem, but it may develop in the delugate tanks. From there the biomatter could be transported and deposited upon the heat exchange surfaces. Chlorine is a common agent used to control this problem in wet systems, but it may promote pitting of aluminum surfaces. Hungarian investigators are testing a deluged HOTERV surface and anticipate solving potential fin biofouling problems by temporary operation at a higher fin temperature while in a dry mode, thus baking the algae (34). McCoy recommends adding a 30-40 ppm concentration of a commercial biocide infrequently rather than smaller amounts on a regular basis (23). Effectiveness and frequency of use would be related to cost.

Fin design and material of the TRANE fin-tube surface varies sufficiently from the HOTERV surface to warrant corrosion/deposition characterization of the TRANE heat exchanger. To this end a model TRANE core has been installed in the Corrosion Deposition Loop to study scaling and corrosion of this heat exchanger type in simulated Kern well water.

Scaling on the TRANE surface is being described as a function of cycles of concentration (up to 6), pH, core temperature, deluge flow rate, and water conditioning (additives). The role played by rinsing in overall scale reduction will be detailed, and efficient methods for periodic scale removal, including rinse pH adjustment, are being examined in the event such procedures are needed. The overall objective will be to develop specific recommendations for operation and maintenance of the ACT wet/dry cooling function.

The material of the model TRANE heat exchanger is not typical of the ACT wet/dry core. Corrosion studies will, therefore, parallel deposition studies using flat plates of representative material. Evidence of pitting and crevice attack at the tube-fin contact, and general corrosion of tubes and fins by Kern well water is being emphasized.

In order to provide similar metal contact at the tube-fin junction, TRANE is fabricating ACT HX fins from 7072 alloy contacting Alclad tubes. The question of general corrosion resistance to Kern water of alloy 7072 will be addressed by exposure of a heated plate of 7072 alloy to deluge in the CDL, and exposure of a 7072 dry plate to the Kern site environment.

Addition of 2 to 3 ppm polyphosphate to makeup well water (22) may be helpful in controlling growth of calcium carbonate crystals. There are many chelating or complexing agents popular in the water treatment field (23). Use of chemical additives for scale control needs additional clarification.

Section 6

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Appendix A

DELUGE WATER PREPARATION AND ANALYSIS

1. Fifty liters of simulated deluge water were made using deionized water (analysis in Table 2-3 of text) and appropriate amounts of the following analytical grade reagents:

+	Na_2SiO_3 $9H_2O$	sodium metalsilicate nonahydrate
+	$CaCl_3$ $2H_2O$	calcium chloride dihydrate
+	Na_2CO_3	sodium carbonate
+	$CaCO_3$	calcium carbonate
+	MgO	magnesium oxide
+	H_2SO_4	sulfuric acid (used to adjust pH to 8.5 and add sulfate)

2. Sampling and Sample Handling:

   Sampling is always done during the CDL deluge cycle to minimize differences occurring between samples during the deluge cycle and samples during the dry cycle. Raw, untreated simulated deluge water samples are taken from the CDL in clean polyethylene bottles and the temperature of the sample is measured and recorded. Conductivity, pH, and alkalinity are measured within minutes after sampling to avoid sample degradation errors. Dissolved solids, chloride, sulfate and silica are determined using the raw untreated sample via standard techniques(1, 2).

   A second deluge water sample is taken in a clean polyethylene bottle to which enough HCl is added to lower the sample pH to approximately one in order to allow a metal ions analysis to be performed later.

3. pH: pH meter and a combination electrode are buffered using commercially available pH 7 and 10 buffers at room temperature (20 to 25°C). Samples are measured as soon as possible after sampling; no attempt is made to compensate for temperature differences between samples and buffers as the error introduced was constant and low.

4. Conductivity: conductivity (in μmhos/cm) is determined with a conductivity bridge and a conductivity cell with cell constant of one. No attempt is made to correct conductivities for temperature.

5. Alkalinity: a Mettler automatic titration and combination electrode buffered at pH 7 and 4 is used to titrate 15 ml of sample to pHs 8.3 (carbonate alkalinity) and 4.5 (bicarbonate alkalinity).

6. Total Dissolved Solids: 200 ml of unfiltered sample are dried in a tared beaker at 100°C and desiccated overnight before reweighing beaker and determining dissolved solids by difference.

7. Chloride: 5 ml of sample are titrated with either 0.0141 N or 0.141 N $AgNO_3$ (commercial preparation) using a Mettler automatic titrator, AgS/S electrode and double-junction reference electrode to an endpoint of 268 mV.

8. Sulfate: 10 ml of sample are diluted to 100 ml; to 25 ml of sample are added a commercial (Hach Co.) preparation of $BaCl_2$ and colloid dispersant. Sulfate in sample is determined by amount of light transmitted versus a blank in an interference filter photometer at 450 mm.

9. Silica: 5 to 10 ml of sample are diluted to 100 ml, 25 of which are treated with commercial reagents (Hach Co.) to form the yellow silicomolybdate complex which is measured at 410 nm on an interference filter photometer.

10. Metal Ion Constituents: sample for metal determinations is collected in a clean polyethylene bottle and acidified with HCl to pH 1 to 2. Al, Ca, Fe, Mg and Na are determined by atomic absorption and inductively coupled (argon) plasma-atomic emission spectroscopy. Metallic constituent data presented in Table 5 and Table 7 of text are the atomic absorption data; in general, the atomic absorption and inductively coupled plasma data agree usually within about 30% in terms of relative accuracy. Silicon was also determined by inductively coupled plasma as a check on the silicomolybdate calorimetric method. (The data presented in the tables are the calorimetric results for silica.)

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Appendix B

ALUMINUM ANODIZING

Square 1100 alloy aluminum test specimens measuring 15 cm on a side and 1.5 mm thick were rinsed with denatured alcohol, etched for 1 min in 5% NaOH at 60 to 65°C, followed by rinses in deionized water, 50% HNO_3, deionized water and denatured alcohol, respectively.

The clean aluminum specimen was then anodized in 5% oxalic acid at 19°C, 16 milliamps cm^{-2} and 50 to 70 volts for 45 min. Immediately upon completion of anodizing, the sample was rinsed free of oxalic acid solution in deionized water and rinsed with alcohol. The coat was sealed in boiling deionized water for 20 min. Coat thickness under these conditions is approximately 16 μm.

A literature survey of corrosion of anodized aluminum reveals little quantitative information on which to base lifetime estimates for dry-cooling towers. There is, however, information on the efficacies of various anodizing processes in certain accelerated tests and the effects of contaminants that are harmful to anodized films.

The most important step to a long-lasting film is to form a compact oxide layer. Sealing the anodized films in boiling water or steam reduces porosity (24), a necessary step to forming an effective protective layer. It is important to keep the pH near neutral in order to form a compact layer. The electrolyte temperature, in relation to the current density, is the most important factor in the production of the cellular structure (25). These cells, along with the surface, must be well rinsed to keep the residue from being sealed in and attacking the film later.

Factors in the sealing step that affect the corrosion resistance are first the method used, with hot water being the most common. When water enters the pore, the aluminum oxide is hydrated and the pore closes. This process leaves room for improvement as it seals only a percentage of the pores, thus leaving others open to contaminants. Other sealants such as lacquers, silicates, nitrates, acetates, ferric oxalates and molybdates have not been shown to be better than the water or steam seal (26). Other additives that may give a more corrosion-resistant film are dichromates and silicones (26, 29). Another important factor in both the anodizing and the sealing is impurities in the working fluids. Small amounts of halides in the solutions can lead to a much shorter life for the anodized coating (30).

On the fully formed film there is no thermally-induced mechanical coating damage even down to -24°C (31). Species that can attack the fully formed film include carbonates, chlorides, copper and mercury. Also in the humid environments with part wet cooling, SO_2 and SO_3 can form acids that attack the film.

The quantitative information that is available indicates that the 5000 series of aluminum offers the most protective oxide layer, primarily due to the high Mg content (32, 33). However, the 1100 aluminum does provide good protection when anodized and fully sealed.

Appendix C

GLOSSARY OF TERMS

ACT	Advanced Concept Test
CDL	Corrosion/Deposition Loop
Cycles	Test run length, 30 min. deluged, 15 min. dried = 45 min. cycle
DCE	Dry Cooling Enhancement (Program)
DCT	Dry Cooling Tower
DIW	Deionized Water
DOE	Department of Energy (U.S.)
EPRI	Electric Power Research Institute
HOTERV	Institute for Energetics (Hungarian)
SEM	Scanning Electron Microscope
TDS	Total Dissolved Solids
WATA	Water Augmented Test Apparatus
2X,3X,4X	Concentration factor of well water at ACT site.