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DRESDEN-2 HYDROGEN WATER CHEMISTRY PROGRAM

AN ASSESSMENT OF PLANT OPERATION DURING INITIAL FUEL CYCLE THROUGH JULY 1984.

EPRI Project RP 1930

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DRESDEN-2 HYDROGEN WATER CHEMISTRY PROGRAM
An Assessment of Plant Operation During Initial Fuel Cycle

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TABLE OF CONTENTS

0. EXECUTIVE SUMMARY

INTRODUCTION

The Dresden-2 BWR has been operating on Hydrogen Water Chemistry since May, 1983 as a means to prevent Intergranular Stress Corrosion Cracking of stainless steel as well as prevent stress corrosion effects in other structual alloys. Materials studies have been conducted at the plant and in the laboratory by several organizations. In addition extensive water chemistry and radiological performance data have been developed to assess the performance of Dresden-2 under these new operating conditions. The key results of all of this work are summarized as follows.

1. Field stress corrosion and electrochemical potential studies provide strong evidence that stainless steel stress corrosion cracking activity at Dresden-2 has been arrested. A series of in situ stress corrosion tests were conducted on furnace sensitized stainless steel with the tests ongoing over about 2000 hours. No cracking was observed in either smooth or IGSCC precracked specimens tested while the plant was operated at 20 ppb O_2 or less and 0.3 uS/cm or less. Electrochemical potential measurements on stainless steel made at the plant for over 3000 hours revealed potentials well below -350 mV (SHE) over 95% of the time. This potential is considered to be a threshold for IGSCC for the conductivity values listed above. These tests at the plant revealed some tolerance for oxygen adn conductivity values higher than those listed above. Coolant oxygen content excursion up to 200 ppb for limited periods of time up to about 15 hours during the constant extension rate test did not result in IGSCC. Electrochemical potentials during these short term excursions did not increase to the values observed under normal operation at 200 ppb oxygen indicating the presence of a memory effect. Presumably. longer term operation at 200 ppb oxygen would have eventually resulted in IGSCC. Perhaps the most revealing test result is the constant extension rate test conducted on a furnace sensitized and IGSCC precracked specimen that had seven hours of test time with 200 ppb oxygen. No IGSCC in addition to that in the precrack phase was noted.

2. The field test results are consistent with extensive laboratory test data which have shown that no crack initiation or growth on pre-existing cracks is expected in sensitized stainless steel under Hydrogen Water Chemistry conditions. This conclusion is based on pipe, crack growth, constant extension rate, and other tests conducted on several heats of material at several different laboratories. Tests also show that no cracking occurs below stainless steel electrochemical potentials of -350 mV (HSE) if conductivity does not exceed 0.3 uS/cm. Additional laboratory studies have shown that there is a strong interaction among oxygen, conductivity and coolant impurity species. Increasing conductivity requires decreasing coolant oxygen content for prevention of cracking. In addition various impurity species have greater or lesser effects at given conductivities. Sodium sulfate is the most severe species that has been identified out of a large number of impurities studied. If only sodium sulfate is present as the impurity, no cracking is expected at 20 ppb oxygen and 0.3 uS/cm conductivity or at 40 ppb oxygen and slightly less than 0.2 uS/cm conductivity.

3. Field water chemistry studies included extensive analyses of coolant oxygen and conductivity as well as ion chromatography to assess the impurities present in the coolant. Results of the studies show that conductivity has steadily improved as has the percentage of time with coolant oxygen below 20 ppb. About 80% of hot operation time (time at above 20% power) was with coolant oxygen below 20 ppb and conductivity below 0.3 uS/cm. A large amount of the remaining time was less than 12 hours where the memory effect described above would prevent cracking. If this is taken into account then 93% of the time is accounted for.

4. In addition, a large amount of the remaining time was for coolant oxygen between 20 and 40 ppb but with coolant conductivity less than 0.2 uS/cm. No cracking is expected for these conditions. Only a few hundred hours of operation were incurred where cracking would not be completely suppressed and even under these conditions reduced susceptibility would be expected.

5. Ion chromatography studies of the coolant at Dresden-2 have shown that under continuous operation conditions, no more than 30 ppb carbonate and no sulfate are present. Thus the species making up the conductivity at Dresden-2 are far less aggresive than the sodium sulfate used to assess conductivity effects in the laboratory studies.

6. Additional in plant and laboratory studies have shown that stress corrosion and/or corrosion fatigue of the other major structural alloys including Inconel 600, carbon steel, and low alloy steel are effectively eliminated by application of Hydrogen Water Chemistry. No effects were found for martensitic stainless steel. Some increase in carbon steel general corrosion rates can be expected but resultant corrosion is well within design tolerances.

7. Addition of Hydrogen Water Chemistry at Dresden-2 has been found to add about 20 man rem per year to the roughly 200 man rem currently incurred. However, the advantages of reduced exposure for IGSCC related repairs more than provides a compensating effect. For example, pipe replacement programs alone account for 1500 to 2500 man rem.

8. At present, no fuels performance data for a water chemistry exactly the same as at Dresden-2 has been developed. However, based on available BWR and PWR data, no harmful effects are anticipated. A special fuels surveillance program has been instituted at Dresden-2 to confirm this with intial data becoming available after this fall's outage.

The available information strongly supports that at Dresden-2 Nuclear Power Station stress corrosion activity of structural alloys, particularly sensitized stainless steel, has been effectively eliminated since the start of the current Fuel Cycle with the Hydrogen Water Chemistry Flowsheet.

1. INTRODUCTION

Intergranular Stress Corrosion Cracking (IGSCC) of Recirculation and other pipe systems has had a significant impact on BWR plant availability. Numerous remedies including alternate pipe alloys and stress improvement treatment that put the pipe welds in compression have been developed and implemented into service. More recently, attention has been focused on Hydrogen Water Chemistry as a means to provide blanket protection against IGSCC for piping, reactor internals and, in fact, almost all structural components. The Dresden-2 BWR has been operating on HWC since March of 1983. A great deal of information has been developed regarding operating plant chemistry, plant materials stress corrosion behavior, and radiation effects in the 17 months of operation at Dresden-2. This document will present the current understanding of this information and how it applies to Dresden-2 operation during the last Fuel Cycle.

The operation of the Dresden-2 plant on the Hydrogen Water Chemistry flowsheet for a full Fuel Cycle is a pioneering step. Testing originally done in Dresden-2 during 1982 showed that the concept of changing the reactor water environment to provide mitigation against IGSCC was technically feasable and commercially practical. Because of these very positive restuls, the Commonwealth Edison Company (CECo) decided to run the Dresden-2 plant full time on the Hydrogen Water Chemistry flowsheet beginning with Fuel Cycle 9, which began in March of 1983. In conjunction with the Electric Power Research Institute and the General Electric Company, an intensive monitoring program was initiated to demonstrate and quantify the benefits of Hydrogen Water Chemistry and measure any potential plant parameters that could be adversely affected, including long term Cobalt-60 induced radiation buildup, crud transport, fuel performance, plant radiation fields, and environs dose rate. This report quantifies the results and effects observed. During Fuel Cycle 9 together with a summary of related laboratory research.

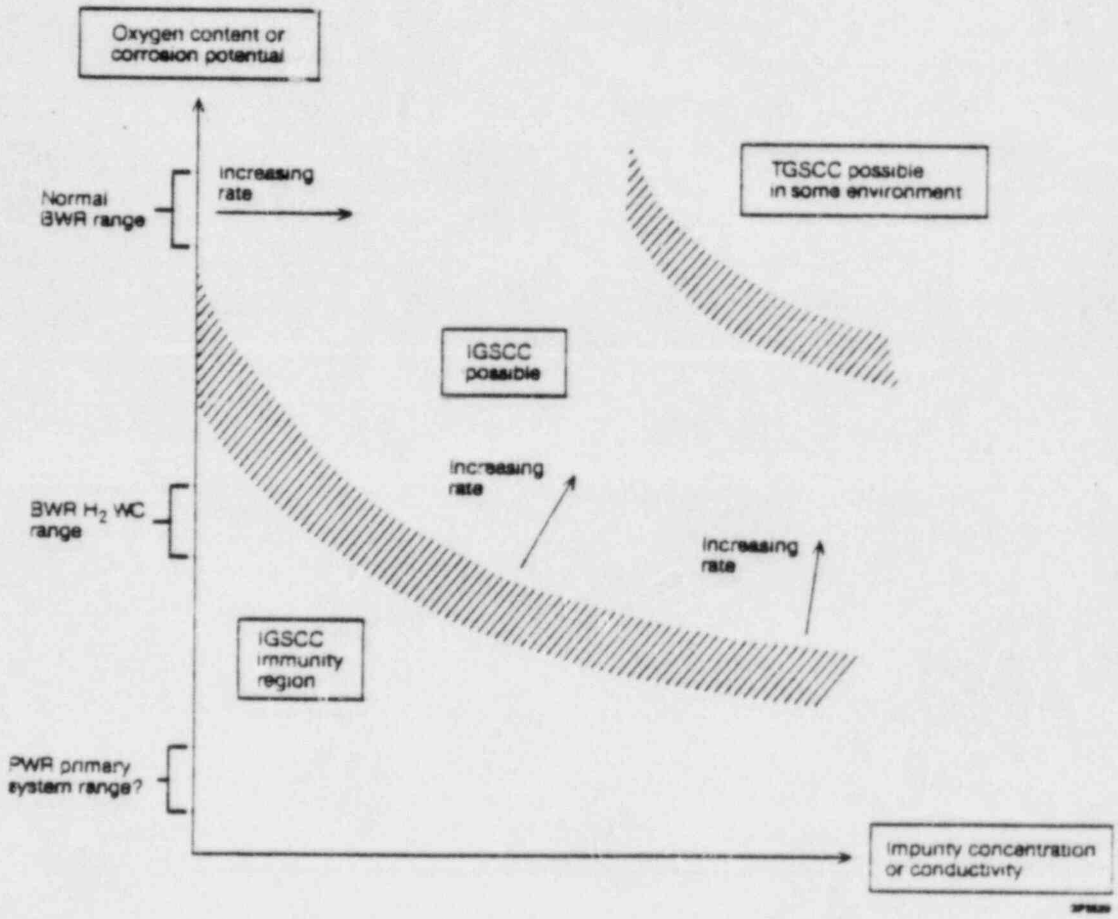
2.0 HYDROGEN WATER CHEMISTRY SPECIFICATION REQUIREMENTS

2.1 INTRODUCTION

The specification for Hydrogen Water Chemistry utilized at Dresden-2 during Fuel Cycle 9 has been established by extensive stress corrosion cracking testing in the laboratory and has been confirmed by testing in the recirculation water at Dresden-2. (1-9) The result of the General Electric laboratory and reactor testing program are detailed in Appendix A of this document. An independant test program at Argonne National Laboratory looking specifically at the effect of impurities on the requirements of the HWC specifications are detailed in Appendix B. The teachings of all of these studies serve as the basis for this specification.

A schematic diagram of the objectives of the specifications are shown in Figure 1. The normal BWR range of oxygen concentration/electrochemical potential and reactor water impurity level lies in a region of susceptability to IGSCC. In Hydrogen Water Chemistry, careful control of water purity and reduction of oxygen content/corrosion potential by feedwater hydrogen addition results in creation of a chemistry in the IGSCC immunity region.

Figure 1



Schematic Summary of the Results of Laboratory Studies of Effect of Impurities on SCC of Stainless Steels

2.2 REQUIREMENTS FOR POWER OPERATION

Table 1 describes the water quality requirements that should be met for power operation (>20% power) to meet the requirements of Hydrogen Water Chemistry. In addition, the verification measurements described below must be made to demonstrate that conditions leading to IGSCC suppression have been achieved.

Ideally, these requirements should be met at all times that the reactor is above ambient temperatures. However, feedwater hydrogen injection is only possible when feedwater is flowing to the reactor vessel. This constraint, coupled with licencing requirements tied to the main steam line radiation monitor, allow injection only above 20% power at Dresden-2. Also, availability of the hydrogen injection system is not 100% and in addition there are also occasions when the H_2 addition is turned off deliberately. The significance of time of operation outside of the range of the specification is discussed in later chapters.

2.3 VERIFICATION MEASUREMENTS

Because of possible subtle variations in IGSC behavior from one plant to another, it is necessary to confirm that the H_2WC requirements defined in Tables 1, in fact, mitigate IGSCC at a specific plant. As soon as the hydrogen injection rate to the feedwater is adjusted to satisfy the steam and recirculating water requirements given in the tables, the measurements described below should be made thereafter at or above 90% power.

1. Stainless Steel Corroison Potential

   The corrosion potential of a Type 304 stainless steel measuring electrode should be determined in recirculating water using the measurement methods described. For a fresh (lightly filmed) stainless steel electrode the measured value is required to be <-350mV(SHE)*. If a higher value is found, the hydrogen injection rate should be increased until the corrosion potential is <-350mV(SHE).

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* The corrosion potentials are calculated on the Standard Hydrogen Electrode (SHE) from measurement against an Ag/AgCl reference electrode of General Electric design as described in Appendix A.

The measurement is required after each refuelling outage. (However, it is recommended that the stainless steel corrosion potential be monitored continuously for diagnostic purposes.)

2. Constant Extension Rate Test (CERT)
   A CERT should be performed on a weld-sensitized Type 304 stainless steel specimen in recirculation system water. Suitable test methods are described in references 1 to 9. A completely ductile failure is required in this test. If any IGSCC is observed, the hydrogen content of the feedwater should be increased by 10 percent increments and the CERT repeated until a completely ductile failure is observed.

   The CERT is required only once, following initial implementation of Hydrogen Water Chemistry. It is recommended that the test be repeated periodically (e.g., once per cycle) to provide proof that IGSCC is still being suppressed during power operation.

TABLE 1
WATER QUALITY REQUIREMENTS AND MATERIALS FOR HYDROGEN WATER CHEMISTRY

PARAMETER AND (UNITS)	FREQUENCY OF MEASUREMENT	NOMINAL VALUE	MAXIMUM (MINIMUM) VALUE
	- REACTOR WATER -		
Dissolved Oxygen (ppb)	Continuous	10	>20, (<5)
Conductivity (uS/cm @25°C)	Continuous	0.2	>0.3
	- MAIN STEAM -		
Dissolved Oxygen (ppm)	Continuous	≤7.0	>7.0

References

1. B. M. Gordon, et al, "Laboratory Studies on Hydrogen Water Chemistry," paper presented at EPRI Seminar on Countermeasures for BWR Pipe Cracking, Palo Alto, CA, November 14-18, 1983.

2. B. M. Gordon, et al, "Mitigation of Stress Corrosion Cracking Through Suppression of Radiolytic Oxygen," Paper #50 presented at the International symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors," Myrtle Beach, South Carolina, August 24, 1983.

3. E. L. Burley, et al, "Oxygen Suppression in Boiling Water Reactors-Phase 2 Final Report, DOE/ET/34203-47, NEDC-23856-7, October 1982.

4. M. E. Indig and J. E. Weber, "Mitigation of Stress Corrosion Cracking in an Operating BWR Via Hydrogen Injection," Paper #125, Corrosion '83, Anaheim. CA, April 18, 1983.

5. B. M. Gordon, et al, "Effectiveness of Hydrogen Additions for Mitigation of Stress Corrosion Cracking in BWR Environments," Paper #20, Corrosion '81, Toronto, Ontario, April 7, 1981.

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7. W. E. Ruther, et al, "Effect of Sulfuric Acid, Oxygen, and Hydrogen in High Temperature Water on Stress Corrosion Cracking of Sensitized Type 304 Stainless Steel," Paper #125, Corrosion '83, Anaheim, CA, April 18, 1983.

8. R. J. Law, et al, "Suppression of Radiolytic Oxygen Produced in BWR by Feedwater Hydrogen Addition," Paper #5 presented at the Third International Conference on Water Chemistry of Nuclear Reactor Systems, Bournemouth, U.K., October 17-21, 1983.

9. R. S. Tunder, et al, "Alternate Alloys for BWR Piping," EPRI NP-2671-LD, October, 1982.

3. PLANT WATER CHEMISTRY OPERATING PRACTICE IMPROVEMENTS

3.1 INTRODUCTION

Water chemistry limits normally used at Dresden 2 prior to the Hydrogen Water Chemistry program were based on federal regulatory requirements (Nuclear Regulatory Commission Technical Specifications) or fuel warranty requirements (General Electric Fuel Warranty Operating Limits) which are adequate to meet safety concerns and avoid gross fuel damage. However, these established limits are much too high to attain the optimum chemistry control under Hydrogen Water Chemistry that will reduce the probability of stress corrosion cracking of stainless steel components. More restrictive water chemistry limits are needed to protect the Nuclear Steam Supply System piping and components from corrosion. General Electric strongly recommended the adoption of internal administrative water quality limits, which are more restrictive than NRC Technical Specifications limits, to be utilized with the Hydrogen Water Chemistry program.

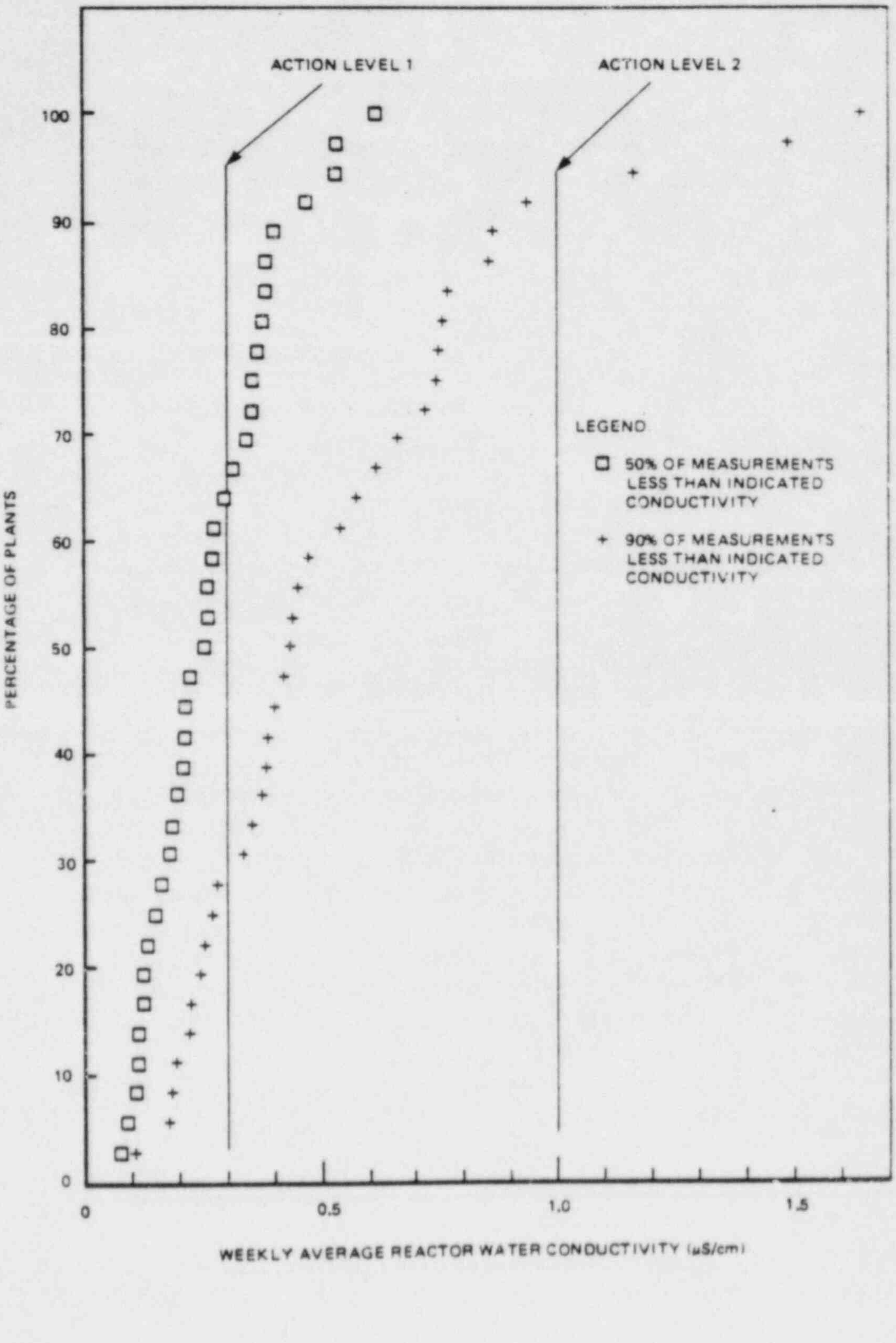
Important chemistry parameters and the limits required to achieve adequate chemistry control are presented in Table 1 and 2. It was recommended that plant management implement and strongly support adherence to the administrative limits.

It is important that the conductivity of reactor water be maintained below 0.2 uS/cm. Conductivity of the condensate-feedwater should be very low. The iron and copper leaving the Condensate Treatment System should also be very low. Close control of the corrosion products present in the feedwater and reactor water and close control of conductivity in these process streams is necessary.

in BWR's during power operation and levels below 0.2 uS/cm can be

Reactor water conductivities of less than 0.3 uS/cm are achievable maintained by using good operational practices regardless of the types or capacities of the Reactor Water Cleanup and Condensate Treatment Systems. Figure 1 shows that over 60 percent of GE-designed BWR's maintained reactor water conductivities less than 0.3 uS/cm for 50 percent of the time during their most recent fuel cycle. Over 20 percent of these plants were able to operate below 0.3 uS/cm for 90 percent of the time.

Figure 1



ACTION LEVEL 1
ACTION LEVEL 2
PERCENTAGE OF PLANTS
0
10
20
30
40
50
60
70
80
90
100
0
0.5
1.0
1.5
WEEKLY AVERAGE REACTOR WATER CONDUCTIVITY (µS/cm)
LEGEND
□ 50% OF MEASUREMENTS LESS THAN INDICATED CONDUCTIVITY
+ 90% OF MEASUREMENTS LESS THAN INDICATED CONDUCTIVITY

Dresden-2, during the previous fuel cycle (Cycle 8) , reported reactor water conductivity ≤ 0.25 uS/cm 50 percent of the time and ≤ 0.42 uS/cm 90 percent of the time, placing it in the middle of the BWR population.

The primary indicator of reactor water purity is conductivity. Non-volatile ionic impurities leaking through the condensate treatment system (or bypassing the Condensate Treatment System and entering the reactor through the Control Rod Drive System) are concentrated in the reactor at some level established by the flow through the Reactor Water Cleanup System and the removal efficiency of that system. Under optimum conditions, reactor water conductivity should be less than 0.2 uS/cm, and reactor water silica concentration should be less than 50 ppb during normal plant operation at power.

Silica entering the primary system usually is associated with condenser cooling water inleakage. Additional silica may be introduced because of incomplete removal of silica by the plant makeup water system or by the use of diatomaceous earth in the radwaste system.

Monitoring for silica in the reactor water and Reactor Water Cleanup System effluent will provide valuable information on demineralizer performance. Monitoring and controlling silica levels will provide control of other anions in general. Since it is impractical to monitor all anions, reactive silica, which is present as a weak anion will if controlled, provide control for other anion impurities including fluoride and carbonate to some extent and certainly for chloride and sulfate.

Low pH conditions contribute to IGSCC and can contribute to increased general corrosion. While not exactly quantified, pH limits have been established to be consistent with the conductivity limits. That is, if the conductivity limits in Tables 1 and 2 are met, the pH will also be under control.

To insure that the water quality of the Dresden-2 reactor stays within the limits required for successful operation under the Hydrogen Water Chemistry program, the operating practices for the plant needed to be optimized.

3.2 DRESDEN - 2 OPERATING PRACTICES

To insure that the water quality of the Dresden-2 reactor stays within the limits required for successful operation under the Hydrogen Water Chemistry Program, the operating practices for the plant needed to be optomized. This section describes the recommendations made to optomize the Dresden-2 water quality related operational practices.

Operating practices at Dresden-2 were assessed by examining plant operating records and conducting interviews with selected plant personnel. The objective of this review was to identify areas where operating practices and procedures needed to be improved to achieve the goal of optimizing reactor water chemistry by reducing the input of corrosion products and other impurities to the reactor.

Highlights of this review were presented to Dresden operations and chemistry personnel during an exit interview in the latter part of 1983. This was supplemented, early in 1984, by a written report.

A summary of the important findings of the review are listed below:

1. Demineralizer resin beds used in the radwaste system should never be returned to the condensate treatment system. If resin beds are to be regenerated and reused, they should be dedicated for use in the radwaste system only.
2. A dedicated individual in operations should be assigned to monitor and supervise the operation and maintenance of the plant demineralizer systems. This should include the demineralizers in the Condensate Treatment Systems, The Reactor Water Cleanup Systems, Fuel Pool Cleanup Systems, Radwaste Systems and the Makeup System.
3. A dedicated chemical engineer or chemist should be assigned the task of collecting and evaluating information on plant water treatment systems. This individual should prepare periodic reports reporting on the performance of the various systems and suggesting changes required to improve performance. Items that should be addressed should include:
    a. Resin Capacity (capacity before and after regeneration if regeneration is practiced).
    b. Cleaning efficiency (frequency of cleaning).
    c. Resin degradation condition (resin has a finite lifetime).
    d. Resin loss and makeup.
    e. New resin quality.
4. Improve resin use.
    a. Upgrade resin specifications.
        (1) Increase capacity requirements.
        (2) Increase friability requirements.
        (3) Increase reporting requirements.
    b. Evaluate the use of resin having an equivalent cation-to-anion resin ratio in the Condensate Treatment System and the Radwaste System.
    c. Purchase premixed resin (equivalent cation to anion resin ratio) for use in the Reactor Water Cleanup System and in the Fuel Pool Cooling and Cleanup System.
5. Enlarge and improve the wet chemistry laboratory facilities.

6. Improve the quality of chemistry measurements.
    a. Separate technician chemistry and health physics functions.
    b. Minimize rotation of chemistry technicians.
    c. Increase technician training.
    d. Assign dedicated technicians to specific tasks.
7. Upgrade sampling and analysis equipment and improve the maintenance of this equipment.
    a. Temperature control of samples.
    b. Temperature control of sample station environment.
    c. Process conductivity versus laboratory conductivity.
    d. Local pH rather than laboratory pH.
    e. Sensitivity for silica.
8. Obtain equipment for measuring organics in various samples. Establish a program to monitor organics in radwaste before it's returned to the condensate storage tank.
9. Perform a more detailed review of sampling, analytical and laboratory facilities, equipment and practices.

3.3 DRESDEN-2 OPERATIONAL CHANGES

A number of changes in operational practices have been made at Dresden during the hydrogen water chemistry program test. Probably the most important change made was the method with which Condensate Treatment System and Radwaste System demineralizers were operated.

Radwaste demineralizer beds were no longer returned to the Condensate Treatment System. All the beds in the Condensate Treatment were replaced over a period of several weeks with new, regenerated resins. The beds were prepared so that there was an equivalent mixture of cation and anion resin, as recommended. When demineralizer beds are exhausted in the Radwaste System, they are discarded as solid waste. The oldest bed in the Condensate Treatment System is transferred to the Radwaste System and it is replaced by a bed of new resin. Resin specifications were suggested and higher quality resin is now being used in the plant. A program for monitoring organic impurities in various plant streams is now being practiced. Other recommendations are in various stages of study or implementation.

The net effect of these changes has been very positive. As is discussed in detail in a later chapter, the reactor water conductivity has met the desired 0.2 uS/cm value for practically all of the Hydrogen Water Chemistry program.

TABLE 1

REACTOR WATER CHEMISTRY LIMITS

PROCESS STREAM AND PLANT OPERATIONAL CONDITION	ADMINISTRATIVE LIMITS	NORMAL OPERATING LIMITS	MAXIMUM OPERATING LIMITS
<u>REACTOR WATER</u>			
1. <u>POWER OPERATION</u>			
CONDUCTIVITY (uS/CM) @ 25°C	.2	1.0	5.0
CHLORIDE (PPB)	20	100	200
pH @ 25°C	6.1 TO 8.1	5.6 TO 8.6	4.9 TO 9.3
SILICA (PPB)	100	200	—
TOTAL COPPER (PPB)	10	20	—
2. <u>STARTUP AND HOT STANDBY</u>			
CONDUCTIVITY (uS/CM) @ 25°C	.2	1.0	2.0
CHLORIDE (PPB)	20	100	100
TOTAL COPPER (PPB)	10	20	—
3. <u>COLD SHUTDOWN</u> *			
CONDUCTIVITY (uS/CM) @ 25°C	1.	2.0	5.0
CHLORIDE (PPB)	50	100	200
pH @ 25°C	5.3 TO 8.6	5.3 TO 8.6	4.9 TO 9.3
SILICA (PPB)	100	200	—
TOTAL COPPER (PPB)	10	20	—
<u>REACTOR WATER CLEANUP EFFLUENT</u>			
CONDUCTIVITY (uS/CM) @ 25°C	.08	.10	.20
SILICA (PPB)	50	100	—
TOTAL COPPER (PPB)	1	2	—

* These limits also apply to fuel storage pools containing fuel that may be reinserted into the reactor; and to suppression pool, condensate storage tank and makeup storage tank water which may be introduced to the reactor.

TABLE 2

CONDENSATE/FEEDWATER CHEMISTRY LIMITS

PROCESS STREAM AND PLANT OPERATIONAL CONDITION	ADMINISTRATIVE LIMITS	NORMAL OPERATING LIMITS	MAXIMUM OPERATING LIMITS
FEEDWATER			
1. POWER OPERATION			
METALLIC IMPURITIES (PPB)	—	15	60
IRON (PPB)			
Insoluble	2.0	10	40
Soluble	.5	1	2
TOTAL COPPER (PPB)	.1	.5	2
OXYGEN (PPB)	25 ± 5	35 ± 15	110 ± 90
CONDUCTIVITY (uS/CM) @ 25°C	.060	.065	.10
2. STARTUP AND HOT STANDBY			
CONDUCTIVITY (uS/CM) @ 25°C	.080	.10	.15
TOTAL COPPER (PPB)	.2	1.	—
CONDENSATE TREATMENT SYSTEM EFFLUENT AND CONTROL ROD DRIVE SEAL WATER			
OXYGEN (PPB)	25 ± 5	35 ± 15	110 + 90
CONDUCTIVITY (uS/CM)	.060	.065	.1
IRON (PPB)			
Insoluble	2.0	10	—
Soluble	.5	1	—
TOTAL COPPER (PPB)	.1	.5	—
CONDENSATE TREATMENT SYSTEM INFLUENT			
CONDUCTIVITY (uS/CM) @ 25°C	.070	.090	—

4. DRESDEN-2 FUEL CYCLE 9 WATER CHEMISTRY

4.1 INTRODUCTION

This section describes water chemistry parameter behavior measured during operation for one Fuel Cycle on the Hydrogen Water Chemistry specification. A statistical analysis of plant behavior with regard to conductivity and dissolved O_2 objectives are discussed in detail. The identity of impurity ions are detailed and the behavior of soluble and insoluble corrosion products with time are detailed.

4.2 CONDUCTIVITY

Reactor water conductivity and oxygen (discussed later) were monitored continuously from November, 1983 thorugh July 15, 1984 using a Keithly Data Acquisition System driven by an IBM Personal Computer. For this program data signals were stored in memory at 5-minute intervals, generating 288 data points on a daily basis. The stored information was downloaded to permanent disk storage every 24 hours. All data have been screened for outage periods, data points discarded, and compiled into the statistical plot shown in Figure 1. Here, the cumulative probability of a reading below a given conductivity (Y-axis) is plotted against conductivity on a logarithmic scale (X-axis). The geometric mean of the data is indicated by the 50% value on the left-hand ordinate; the standard deviations on the right-hand ordinate are in increments of plus or minus 1 sigma above or below the mean. As of this writing, the geometric mean for the reporting period is 0.0105 uS/cm; the reator water conductivity has been below 0.2 uS/cm 98% of the time. The station has clearly met and exceeded the goal for the Fuel Cycle to maintain the conductivity below 0.3 uS/cm 90% of the time, with a target value of 0.2 uS/cm. Figure 2 shows that a typical month in 1984, reflecting incorporation of all key operating practice recommendations, resulted in even better statistics.

For comparative purposes, the average conductivities for Fuel Cycles 3-9 are shown below

FUEL CYCLE	AVERAGE CONDUCTIVITIES
3	0.331 uS/cm
4	0.185
5	0.302
6	0.246
7	0.246
8	0.250
9	* 0.105
3-8	0.269

* Through July 15, 1984

The data for Cycles 3-8 represent weekly average conductivities provided by Commonwealth Edison to General Electric as part of the Fuel Warranty documentation. While not as extensive as the data base for Fuel Cycle 9, the improvement in Cycle 9 operation is readily apparent. This improvement is not a direct result of the implementation of hydrogen water chemistry, but of a series of implemented recommendations aimed at improving overall water quality, which would be successful for a plant not operating on a hydrogen water chemistry flowsheet.

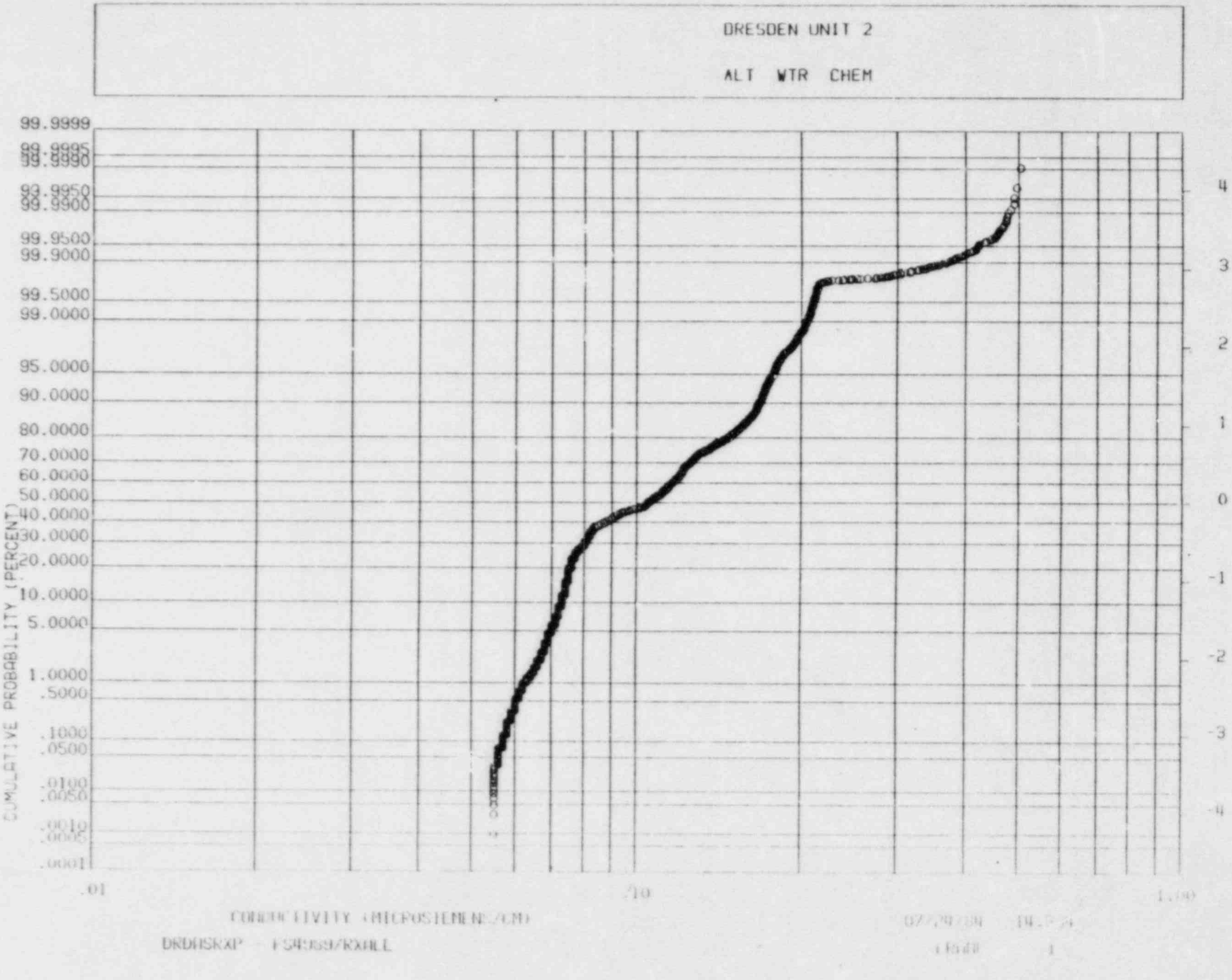


FIGURE 1

REACTOR WATER CONDUCTIVITY COMULATIVE DATA FOR CYCLE

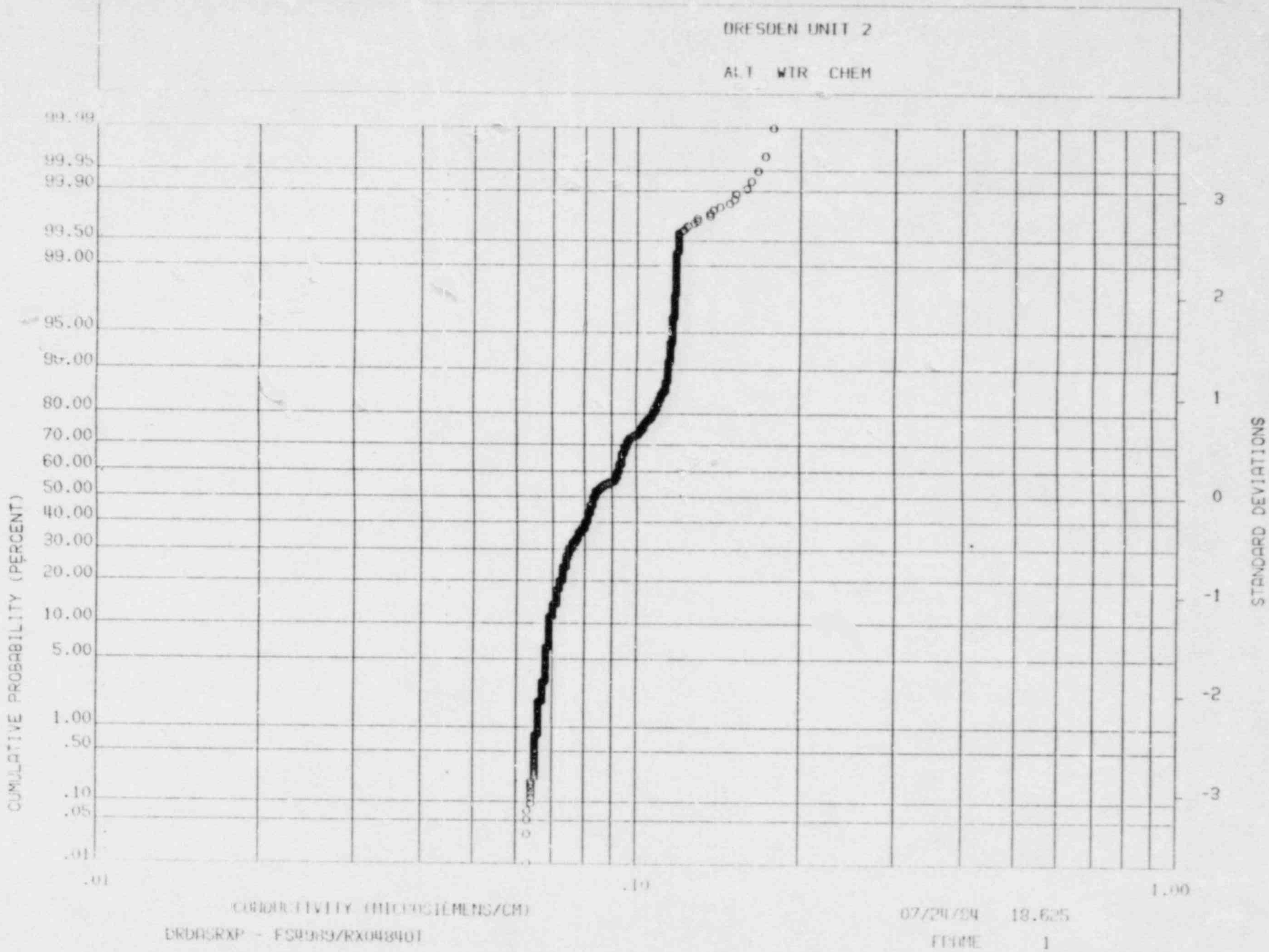


FIGURE 2
REACTOR WATER CONDUCTIVITY DATA FOR TYPICAL MONTH IN 1984 (4/84)

4.3 CORROSION PRODUCT BEHAVIOR

The implementation of hydrogen water chemistry in a BWR provides a more reducing environment in both the feedwater and the reactor water. In the feedwater, this is primarily the result of increased dissolved hydrogen concentrations (1.0-1.5 ppm with hydrogen addition, 1-2 ppb without hydrogen addition), while in the reactor water, it is the result of lower dissolved oxygen concentrations. As a part of the chemistry monitoring program at Dresden-2 for Fuel Cycle 9, feedwater and reactor water corrosion products were monitored from July, 1983, through March, 1984. In the feedwater, soluble and insoluble corrosion products were collected continuously, with samples changed at roughly three-day intervals. Each sample fraction was analyzed at Vallecitos Nuclear for Fe, Cu, Ni, Co, Zn, Cr, and Mn. Roughly three reactor water samples were collected each week. They were first analyzed at the site for gamma-emitting radioisotopes, and then transported to Vallecitos for the same chemical analyses as the feedwater samples.

The dominant impurity in the Dresden-2 feedwater is insoluble iron. Figure 3 shows the concentration of insoluble Fe as a function of time for the Cycle 9 reporting period. The 20-ppb spikes are the result of several condensate demineralizer changeouts over a short interval; the 40-ppb spike encompasses an orderly shutdown for pipe crack inspection and the restartup of the reactor. No long-term adverse consequences of hydrogen addition are evident. The time-base plots for the other elements that were analyzed all show similar patterns, with no element showing an upward trend with time. The concentration of the other insoluble metals is generally less that 0.1 ppb. The table below shows the average concentration of insoluble iron for Cycle 9 and each of the preceding 6 Fuel Cycles.

FUEL CYCLE	AVERAGE IRON CONCENTRATION (ppb)
3	2.47
4	2.50
5	4.04
6	6.49
7	4.15
8	2.40
9	5.03

The Cycle 9 data base is much more extensive than the Fuel Warranty information supplied for Cycles 3-8. It should be noted that the Cycle 3-8 data does not include startup and shutdown sampling data. Elimination of the startup and shutdown samples from the Cycle 9 data base would reduce the average to less than 3 ppb.

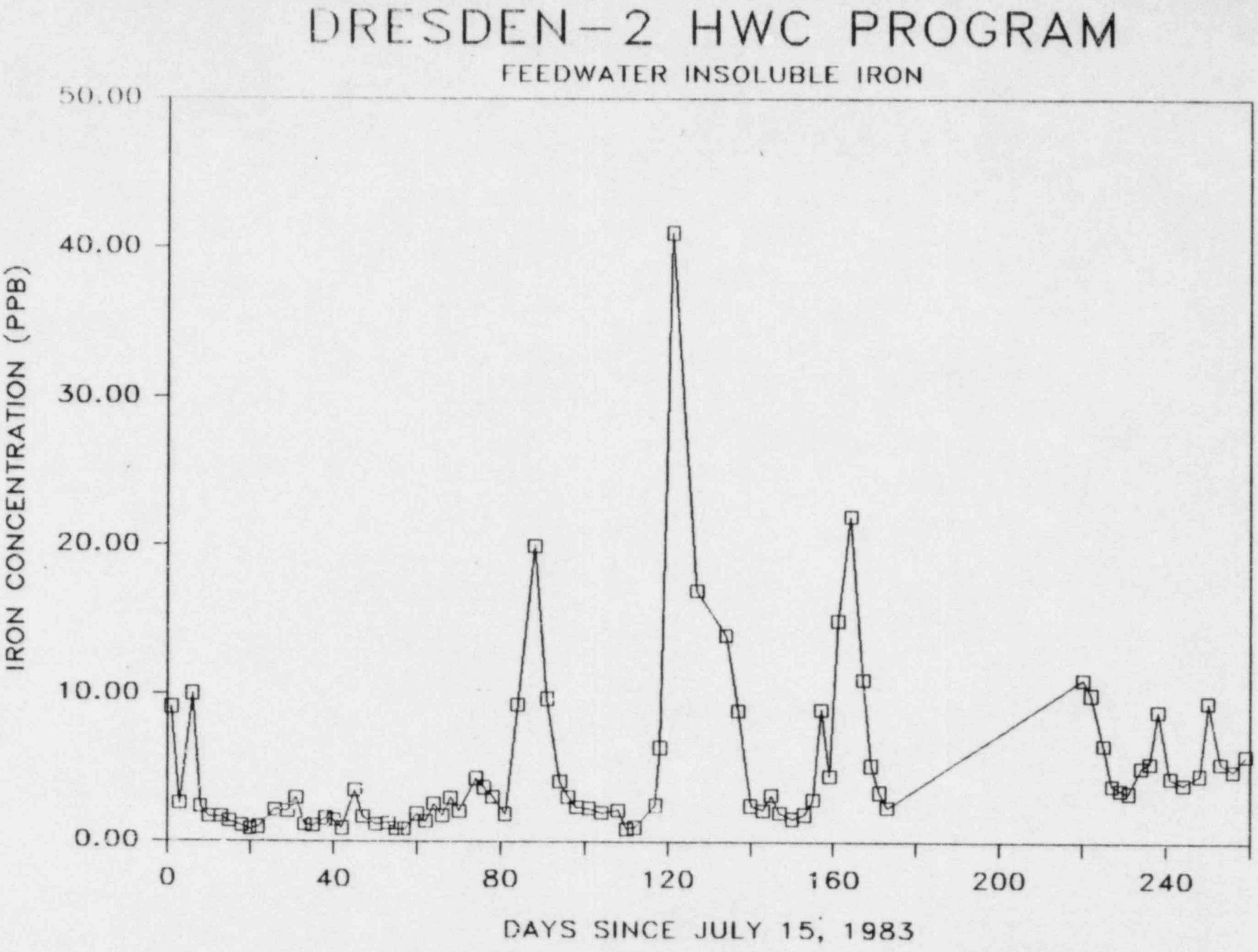
Of the soluble species that were monitored in the feedwater, Cobalt is the element of greatest concern because of its activation to Co-60 in the reactor core and accompanying potential for radiaton buildup. Figure 4 shows the concentration of soluble cobalt in the feedwater as a function of time. The downward and stable trend of cobalt is readily apparent. This trend pattern is also observed for the other elements that were analyzed. Because of the operational practices changes to the condensate treatment system that were implemented during Cycle 9, it cannot be explicitly concluded that the trend is a result of hydrogen water chemistry. Nonetheless, there appear to be no adverse consequences of hydrogen water chemistry for soluble species in the feedwater. Cobalt monitoring in the feedwater is not required in the fuel warranty documentation, so there are not comparable data for Cycles 3-8. The 7 ppt average for soluble cobalt is consistant with General Electric data from other deep bed plants which are not operating on hydrogen water chemistry.

Monitoring of metallic impurities in reactor water is not required in the General Electric Fuel Warranty Documentation. It is still imperative to study the time-dependent behavior of these impurities under conditions of hydrogen water chemistry. Figure 5 shows the concentration of reactor water in insoluble cobalt as a function of time. The data points prior to October, 1983 (roughly day 76) should be disregarded owing to sampling difficulties (lack of adequate flow rates in the sample lines). While there is considerable scatter in the 10-200 ppt range, the average value of 40 ppt agrees very well with measurements taken at other BWR's. There is no definitive upward or downward trend in the data for cobalt or any of the elements that were analyzed. The large spikes occur at the same time periods as the insoluble iron transients in the feedwater (Figure 3).

The gamma counting of the reactor water corrosion product samples revealed no unusual isotopes during the reporting period. Each sample contained the usual suite of activation products, i.e. Co-60, Co-58, Fe-59, Mn-54, Zn-65, and Cr-51. Most spectra were completely devoid of fission product isotopes. Of the activation products, Co-60 was clearly the most dominant isotope in both soluble and insoluble sample fractions. Figure 5A shows the concentration of insoluble Cobalt-60 in reactor water. Again, data prior to October should be disregarded. As in the plot for the insoluble cobalt precursor, there are no indications for an upward nor a downward trend in the concentration of the isotope. Values between 0.1 and 0.2 uCi/l are consistent with data from other BWR's.

Figure 6 shows the concentration of soluble cobalt in the reactor water as a function of time. The downward trend is readily apparent. The concentration of cobalt has steadily decreased from 100 ppt at the beginning of the measurement campaign to 40 ppt at the end of the sampling period. Downward trends were also obeserved for the remaining elements that were analyzed. Figure 7 shows the concentration of soluble Co-60 in reactor water as a function of time. Here it appears that the Co-60 concentration is increasing with time, from typial values of 0.1 uCi/l at the beginning of the sampling period to 0.2 uCi/l at the end of the campaign. This behavior is consistent with recent General Electric theories on cobalt transport, and does not suggest that the increase is a result of hydrogen water chemistry. Essentially, the theory predicts that with higher feedwater purity and reactor water purity, lower elemental cobalt would be expected. Concurrently, with reduced cobalt input via the feedwater, dissolution of fuel deposit cobalt would provide a higher fraction of the cobalt; thus, the higher Co-60.

Summarizing the corrosion product data, we have not seen any indication that hydrogen water chemistry has caused any detrimental change in the soluble and insoluble corrosion product transport in the feedwater or the reactor water. In the feedwater, insoluble spikes are common to all BWR's, and clearly will propagate to the reactor water. The downward trend in feedwater solubles, we feel, is the result of a gradual implementation of good operational practices centered around the management of the condensate treatment system. The concentrations of the impurities in the feedwater and reactor water are consistent with data from other deep bed plants.



DRESDEN-2 HWC PROGRAM

FEEDWATER INSOLUBLE IRON

FIGURE 3

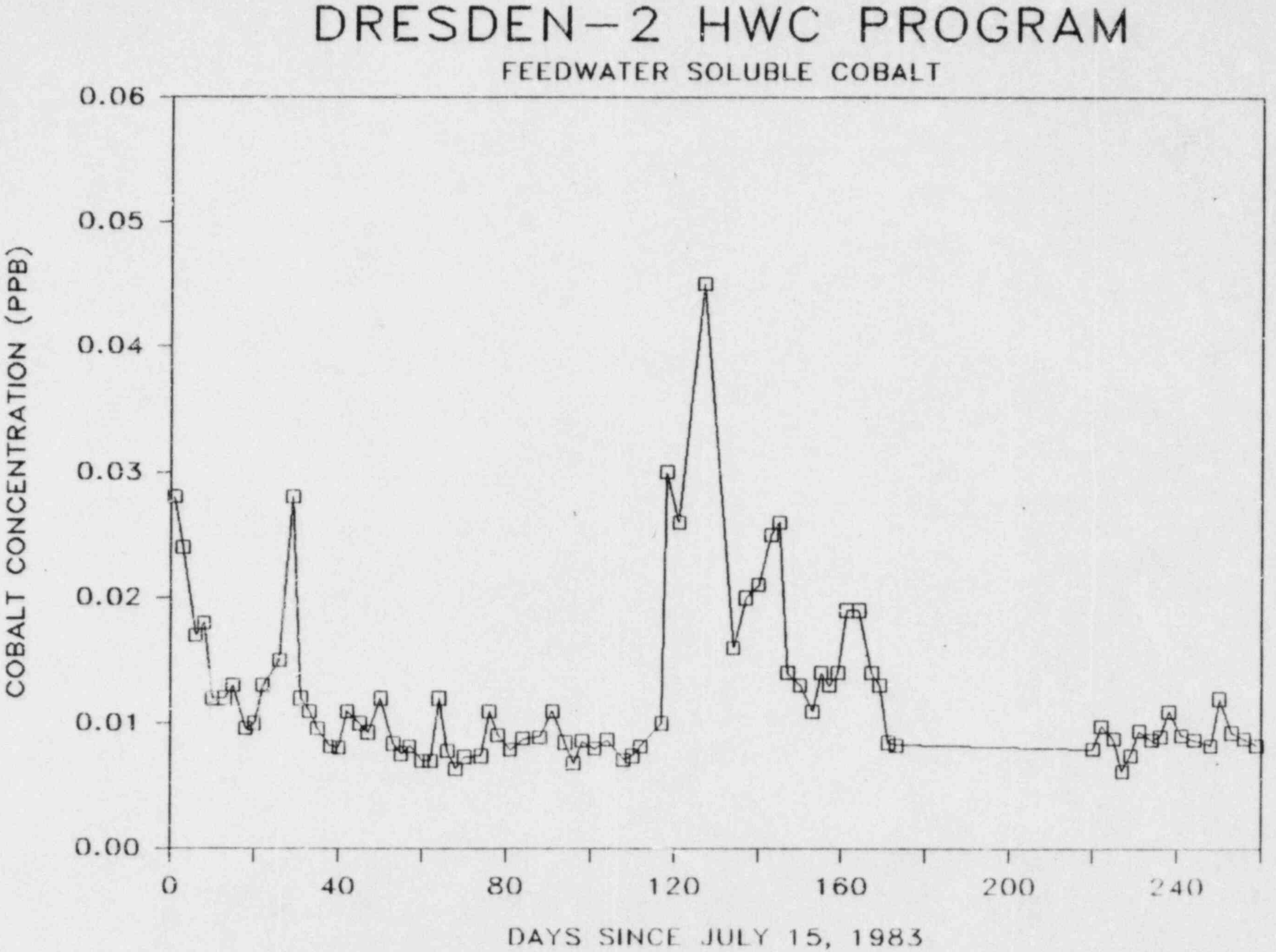

DRESDEN-2 HWC PROGRAM
FEEDWATER SOLUBLE COBALT
COBALT CONCENTRATION (PPB)
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0
40
80
120
160
200
240
DAYS SINCE JULY 15, 1983

FIGURE 4

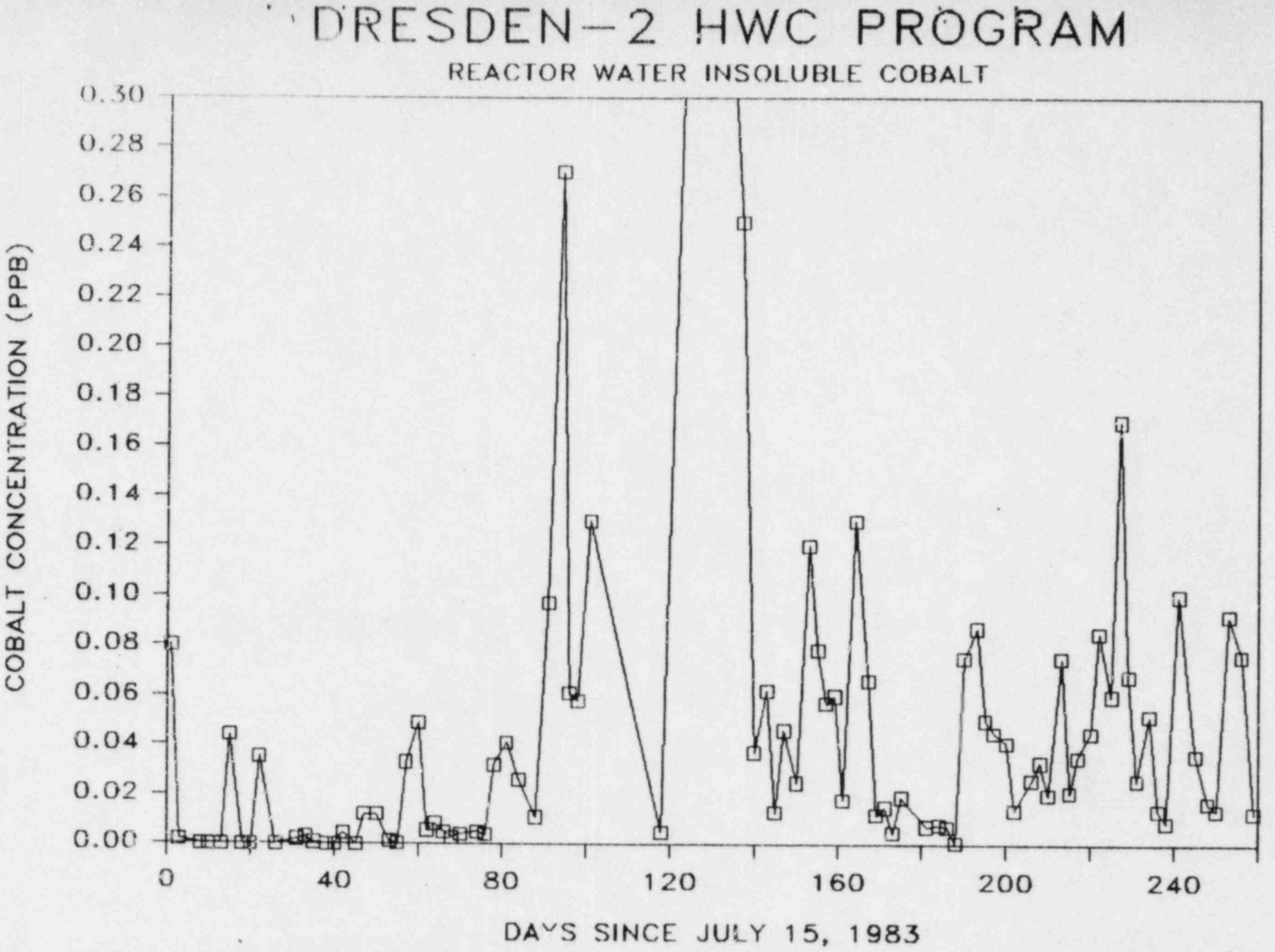

DRESDEN-2 HWC PROGRAM
REACTOR WATER INSOLUBLE COBALT
COBALT CONCENTRATION (PPB)
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
40
80
120
160
200
240
DAYS SINCE JULY 15, 1983

FIGURE 5

DRESDEN-2 HWC PROGRAM

REACTOR WATER INSOLUBLE COBALT-60

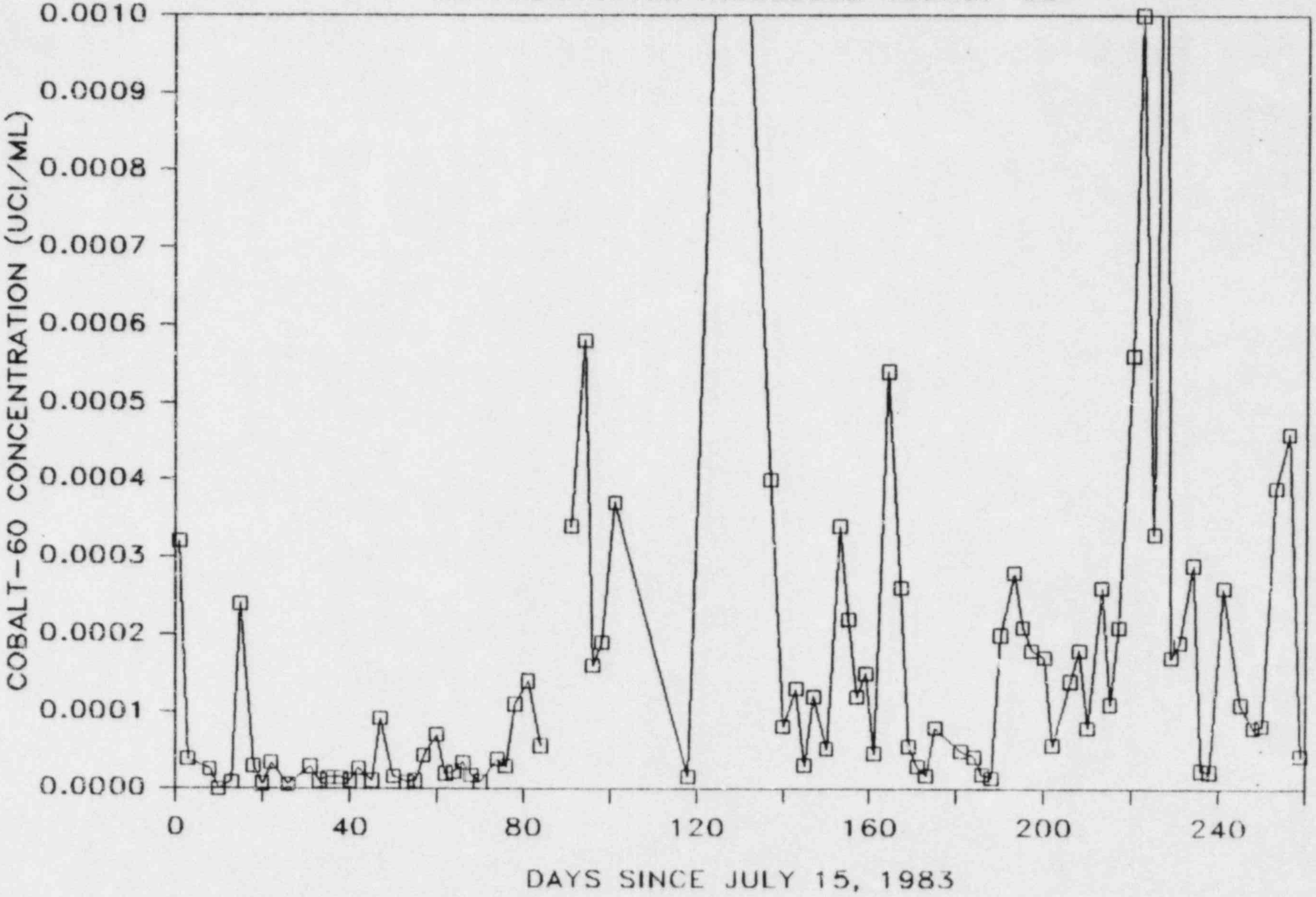


FIGURE 5A

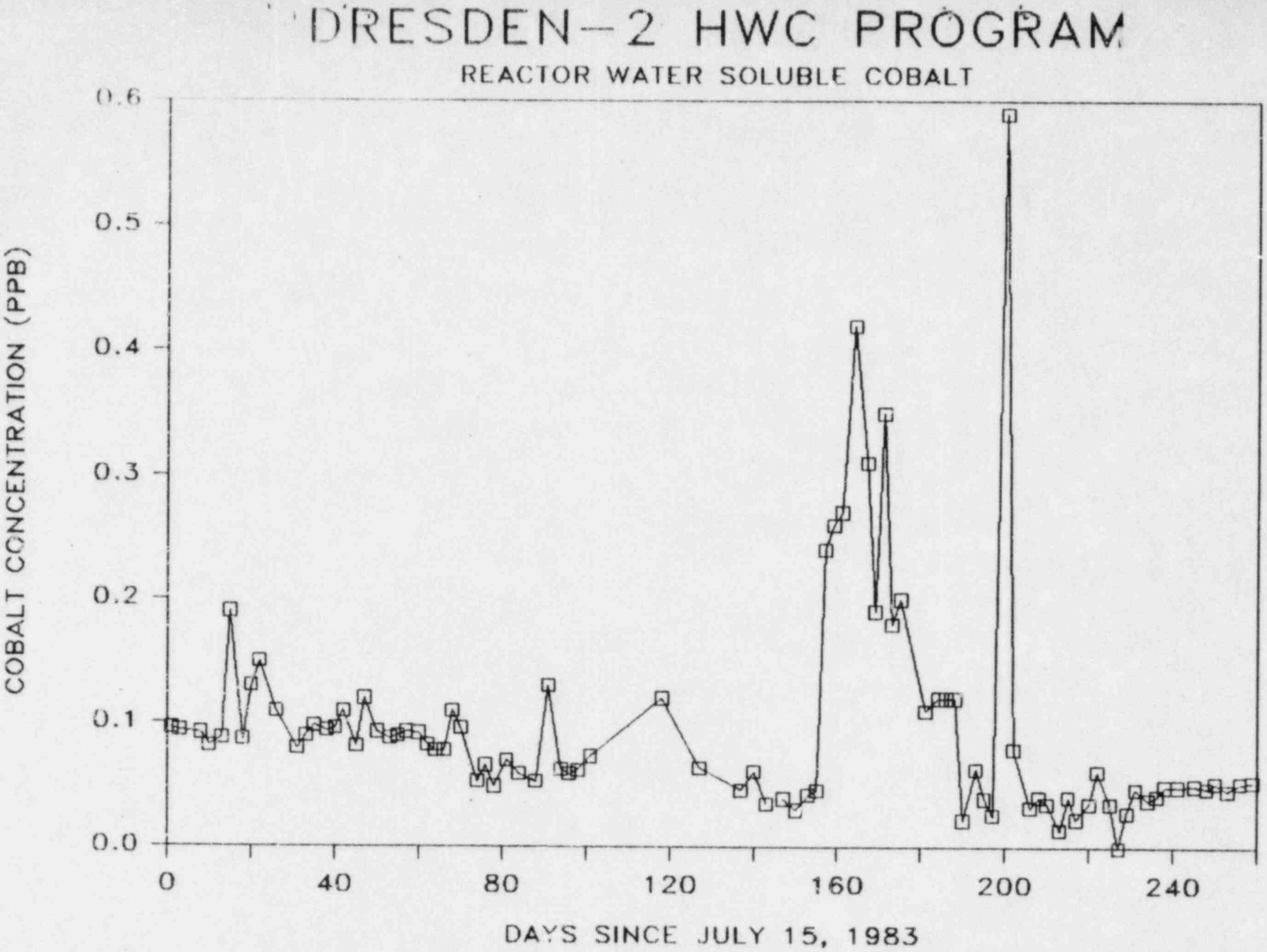

DRESDEN-2 HWC PROGRAM
REACTOR WATER SOLUBLE COBALT
COBALT CONCENTRATION (PPB)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
40
80
120
160
200
240
DAYS SINCE JULY 15, 1983

FIGURE 6

DRESDEN-2 HWC PROGRAM

REACTOR WATER SOLUBLE CO-60

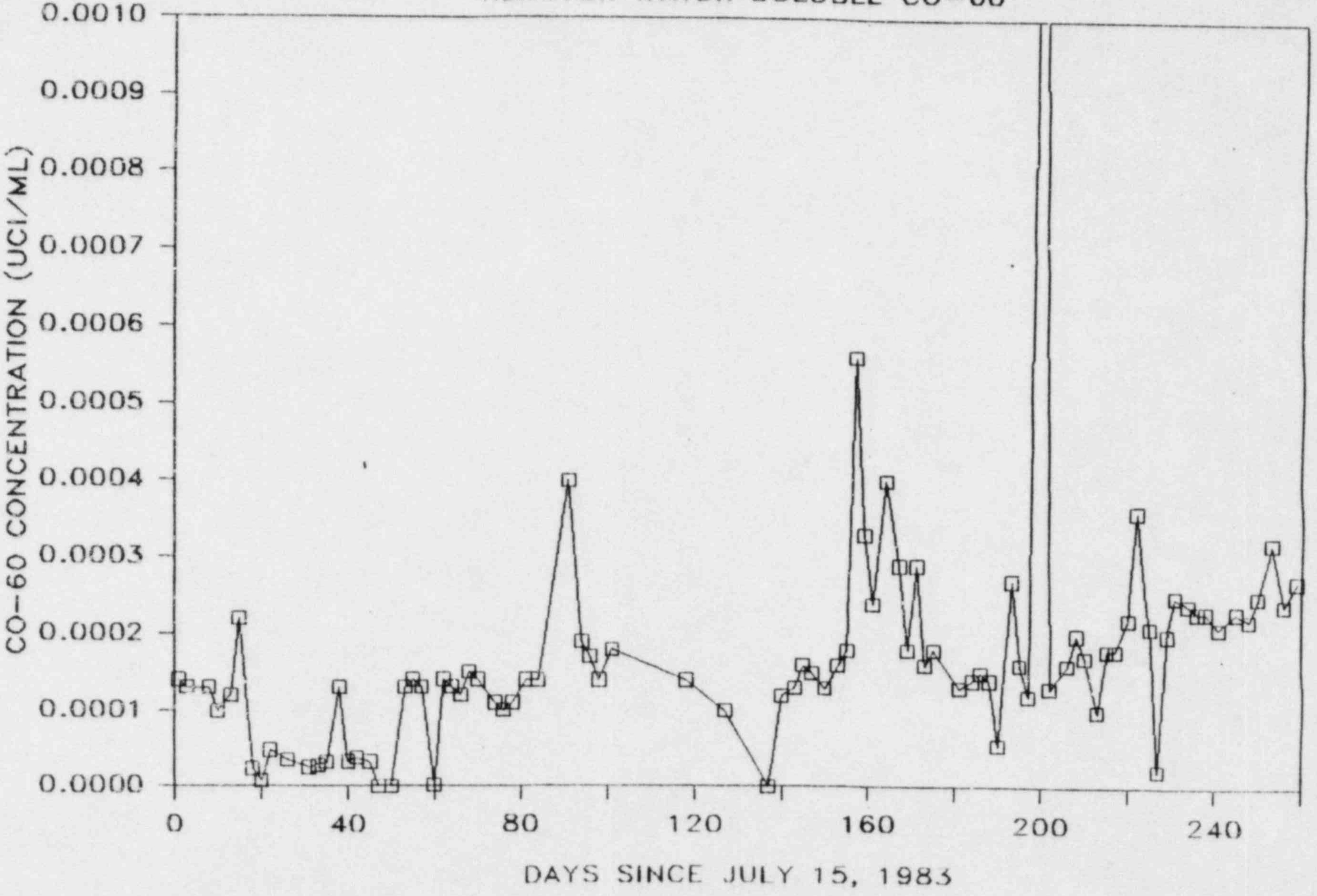


FIGURE 7

4.4 MEASURED OXYGEN CONCENTRATION

At Dresden-2, primary coolant dissolved oxygen concentrations range between 70 and 280 ppb under normal operating conditions (i.e., without hydrogen addition). There is a power dependence on these values: the higher the power, the greater the concentration of dissolved oxygen (more radiolytic oxygen production). When the hydrogen addition system is operating, the concentration of dissolved hydrogen in the feedwater largely determines the concentration of dissolved oxygen in the reactor water recirculation system. For a given power level, the greater the concentration of feedwater hydrogen, the lower the concentration of dissolved oxygen in the recirculation system. The power dependence is also maintained. For a given concentration of hydrogen in the feedwater, the greater the power, the greater the dissolved oxygen concentration in the recirculation system.

The data base for the dissolved oxygen measurements includes periods of high and low power operation, and periods when the hydrogen addition system was turned off and on. The hydrogen addition system was turned off/on many occasions for a variety of reasons; among these were maintenance activities on the hydrogen addition system itself, maintenance in other areas of the plant where there were high N-16 radiation levels due to hydrogen addition, and fires in the offgas treatment system in which the hydrogen addition system was shutdown to extinguish the fires. In addition, during reactor startups and shutdowns, hydrogen addition is not used below 200 MWe (~25% power).

From initial startup in March, 1983 until the end of October, 1983 the dissolved oxygen concentrations in reactor water were recorded manually. From November, 1983 until the present, reactor water oxygen concentration was measured with an automatic data aquisition system at five minute intervals. Figure 8 shows the cumulative statistics for the March through October period and Figures 9 through 17 show statistical plots of each individual month of data for November, 1983 through July, 1984. Figure 18 shows the cumulative statistics for 1983 and 1984 and Figure 19 shows the cumulative statistics for all of 1984.

The data presented in Figures 8 through 19 are presented in a Weibull statistics format. To find the cumulative time the variable (oxygen concentration) is below a certain percentage, find the value on the "X" axis and read the corresponding percentage on the "Y" axis corresponding to the data point.

A summary of the statistics presented graphically in Figures 8 through 19 is summarized in Table 1. The data is presented by month for cumulative time of reactor water oxygen less than 20 ppb, 30 ppb and 40 ppb. Also included are the monthly statistics from the plant data files showing the percentage of time the hydrogen addition system was operating. When the injection system is operating, it will significantly reduce the oxygen concentration in the reactor water. This fact is shown when the statistics of reactor water oxygen concentration less than 40 ppb are compared against the plant statistics for hydrogen addition system availability. The values are essentially identical for any given monthly time period and show that the overall injection system availability is about 87%. During the early part of the Fuel Cycle (March - December, 1983), the injection system, when on, did not control the oxygen concentration as well as it did during the 1984 time period. The 1984 statistics reflect hardware inprovements in the control system implemented in late 1983. For example, in early 1983 the injection system was "on" about 90% of the time but oxygen was controlled to less than 20 ppb for only 74% of the time. However, for the 1984 period the injection system was available for about 90% of the time and the oxygen was controlled below 20 ppb for 86% of the time.

It is worthwhile to investigate the nature of the time the reactor water was greater than 20 ppb oxygen because of the corrosion potential "memory effect" presented in Chapter 3. This effect shows that if the oxygen level rises to 200 ppb, the corrosion potential stays below the critical value for IGSCC for 10 hours. The statistical data base shows that of the cumulative time, the reactor water was above 20 ppb, greater than 70% of that time was less than 10 hours in any given day. This analysis implies that of the total cumulative time elapsed since startup of Dresden-2 in March, 1983, over 93% of the time has been in the corrosion potential region that is "immune to IGSCC".

Figure 20 shows the cumulative data for oxygen concentration in the main steam phase for July, 1983 to July, 1984 is similar to the reactor water oxygen. This data was not recorded automatically and represents one data point per day.

TABLE 1. CUMULATIVE STATISTICS FOR OXYGEN CONCENTRATION IN REACTOR WATER

	DISSOLVED OXYGEN (PPB) CUMULATIVE % TIME BELOW INDICATED VALUE			% TIME HYDROGEN INJECTION
	<20	<30	<40	
AP/MAR83				88
UL83				87.9
AUG83	74	80	82	93.6
SEP83				96.8
OCT83				89.4
NOV83	70	76	80	80.7
DEC83	52	70	78	82.6
JAN84	91	93	96	91.4
FEB84	75	77	78	79.1
MAR84	86	92	92.5	93.4
APR84	91	93	94	93.3
MAY84	89	93.5	94	95.3
JUN84	85	89	89	90.7
JUL84	91	92	92.5	----
ALL 83/84	78	85	87	----
ALL 84	86	90	91	----

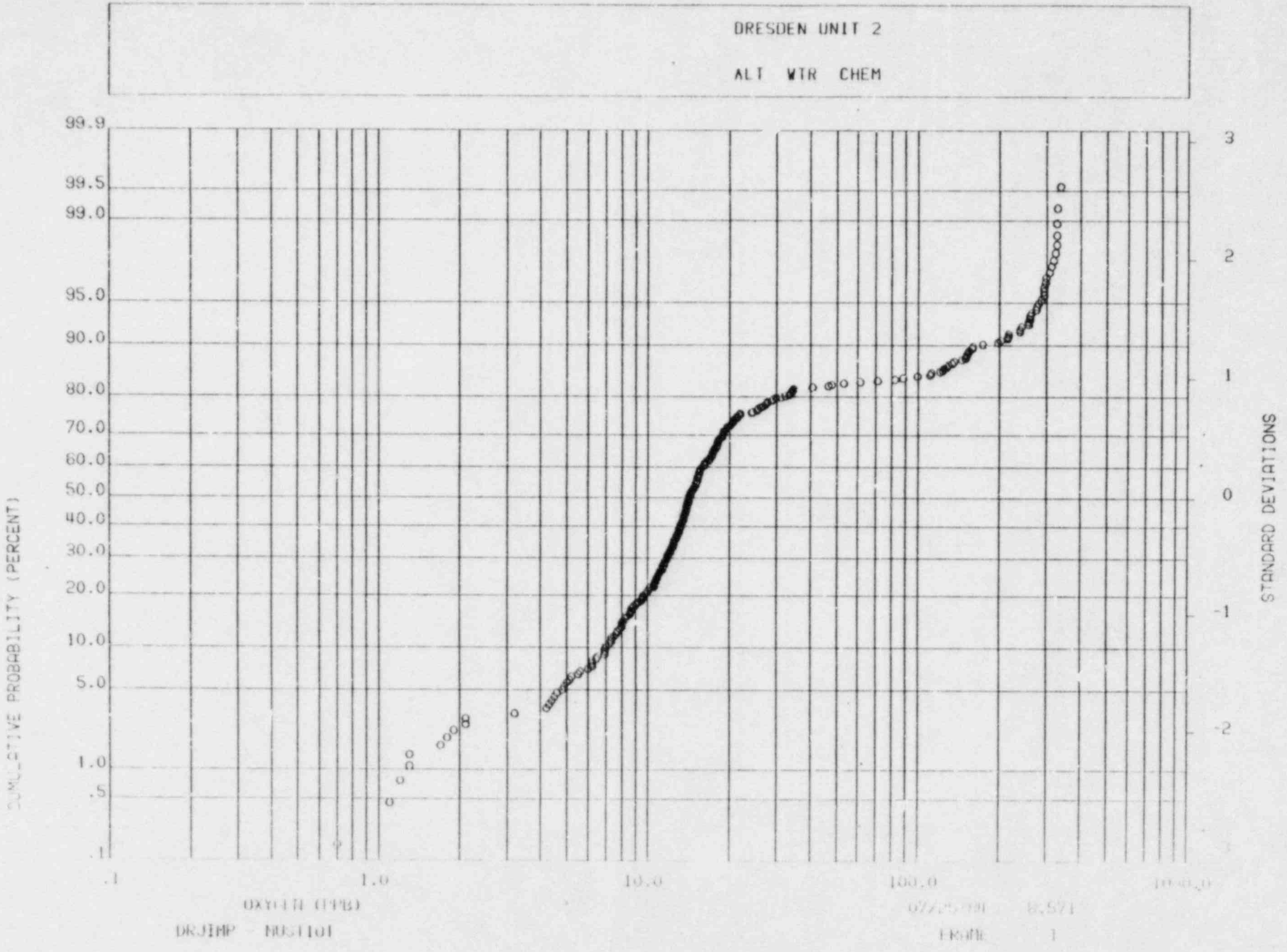


FIGURE 8. CUMULATIVE DAILY OXYGEN MEASUREMENTS FOR MARCH TO OCTOBER, 1983

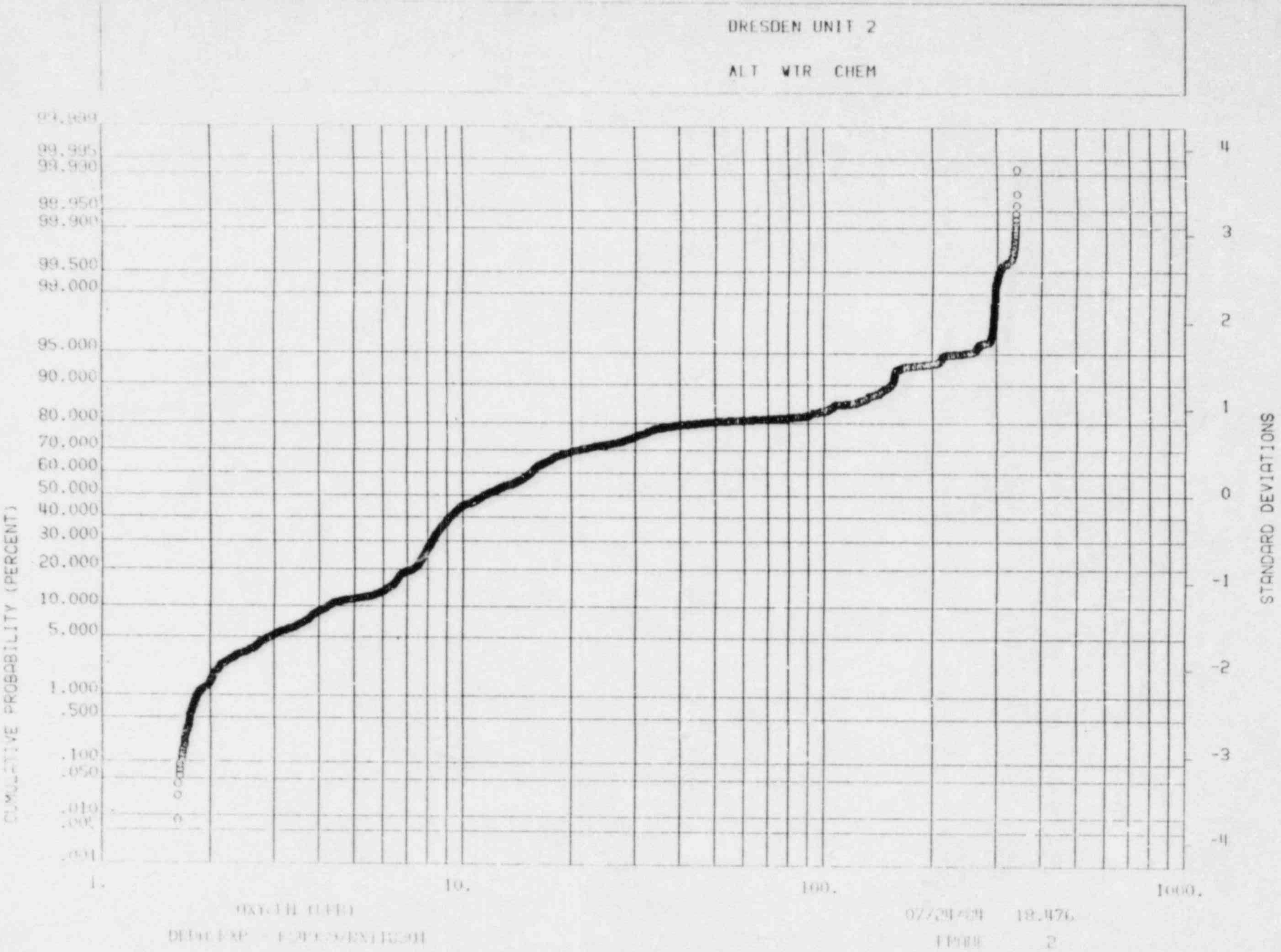


FIGURE 9. NOVEMBER 1983 OXYGEN MEASUREMENTS

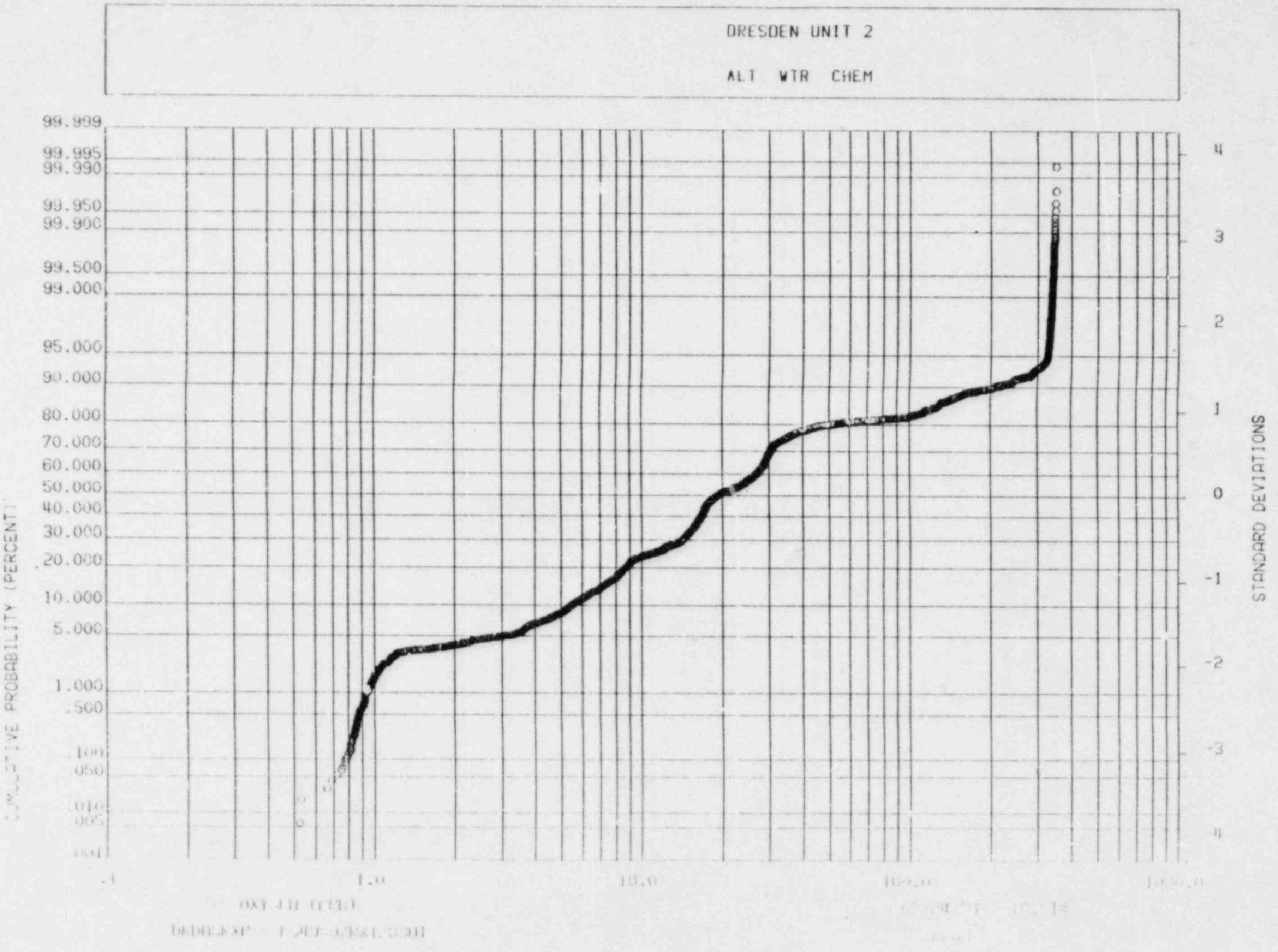


FIGURE 10. DECEMBER 1983 OXYGEN MEASUREMENTS

FIGURE 11. JUANUARY 1984 OXYGEN MEASUREMENTS

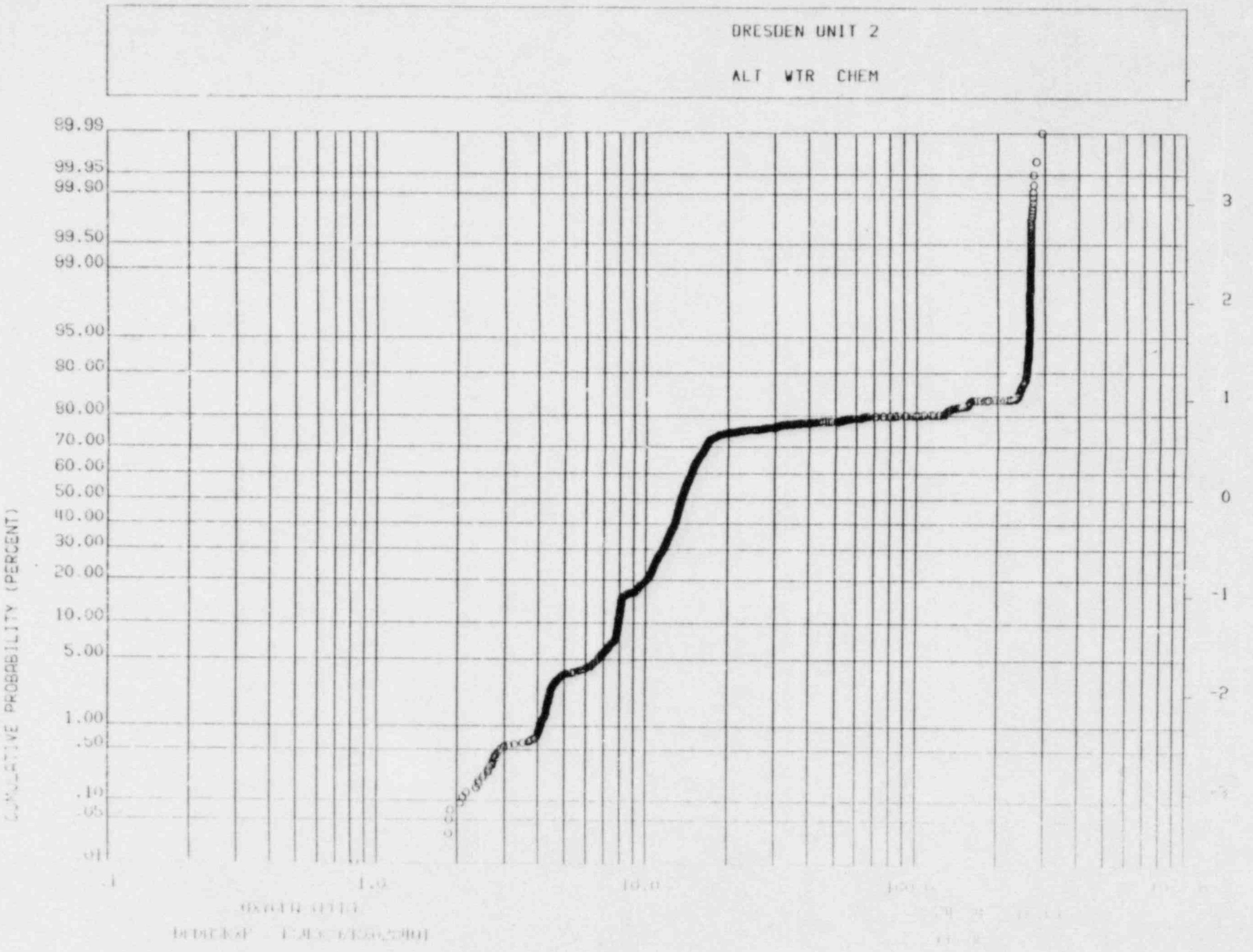


FIGURE 12. FEBRUARY 1984 OXYGEN MEASUREMENTS

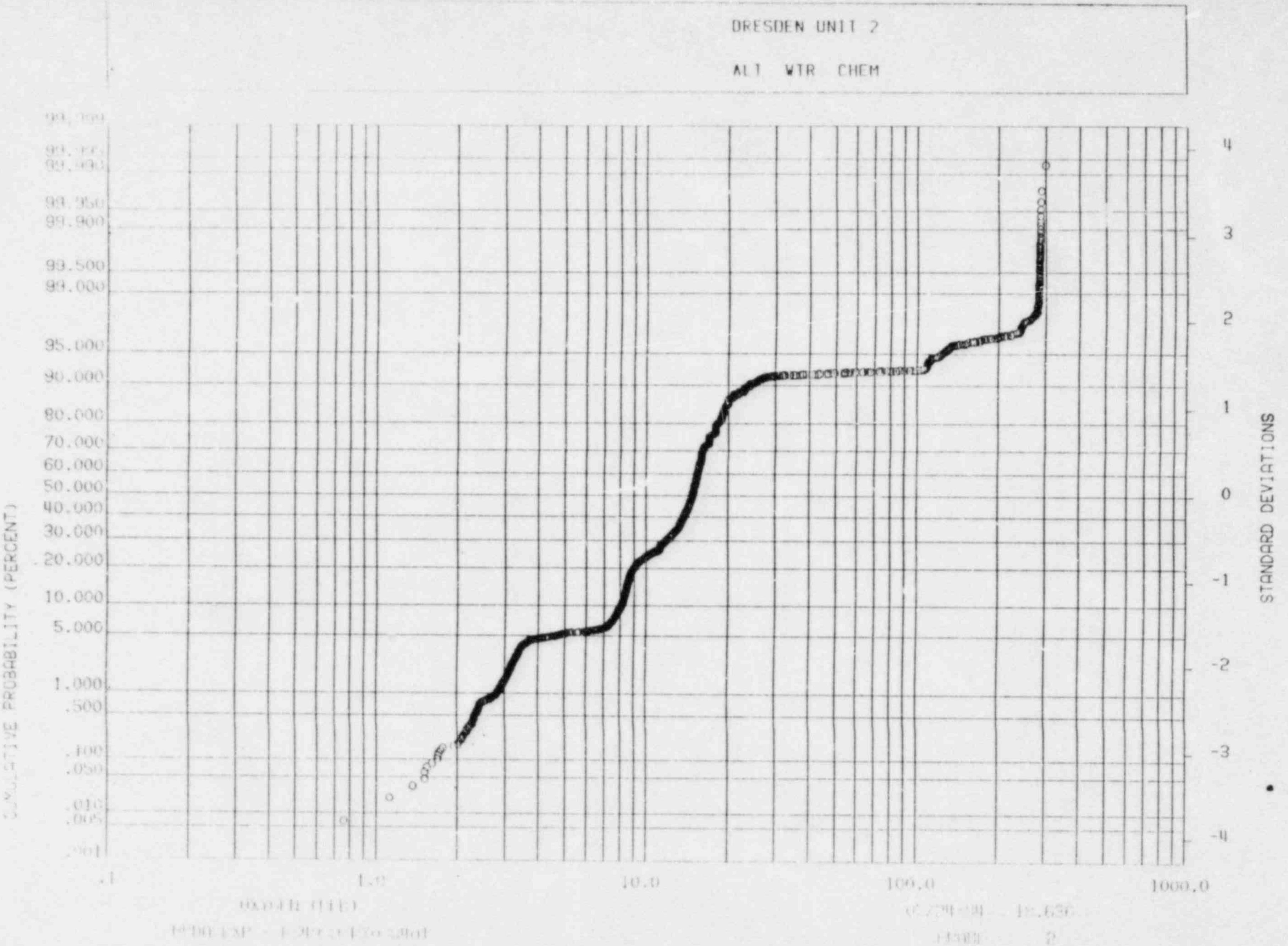


FIGURE 13. MARCH 1984 OXYGEN MEASUREMENTS

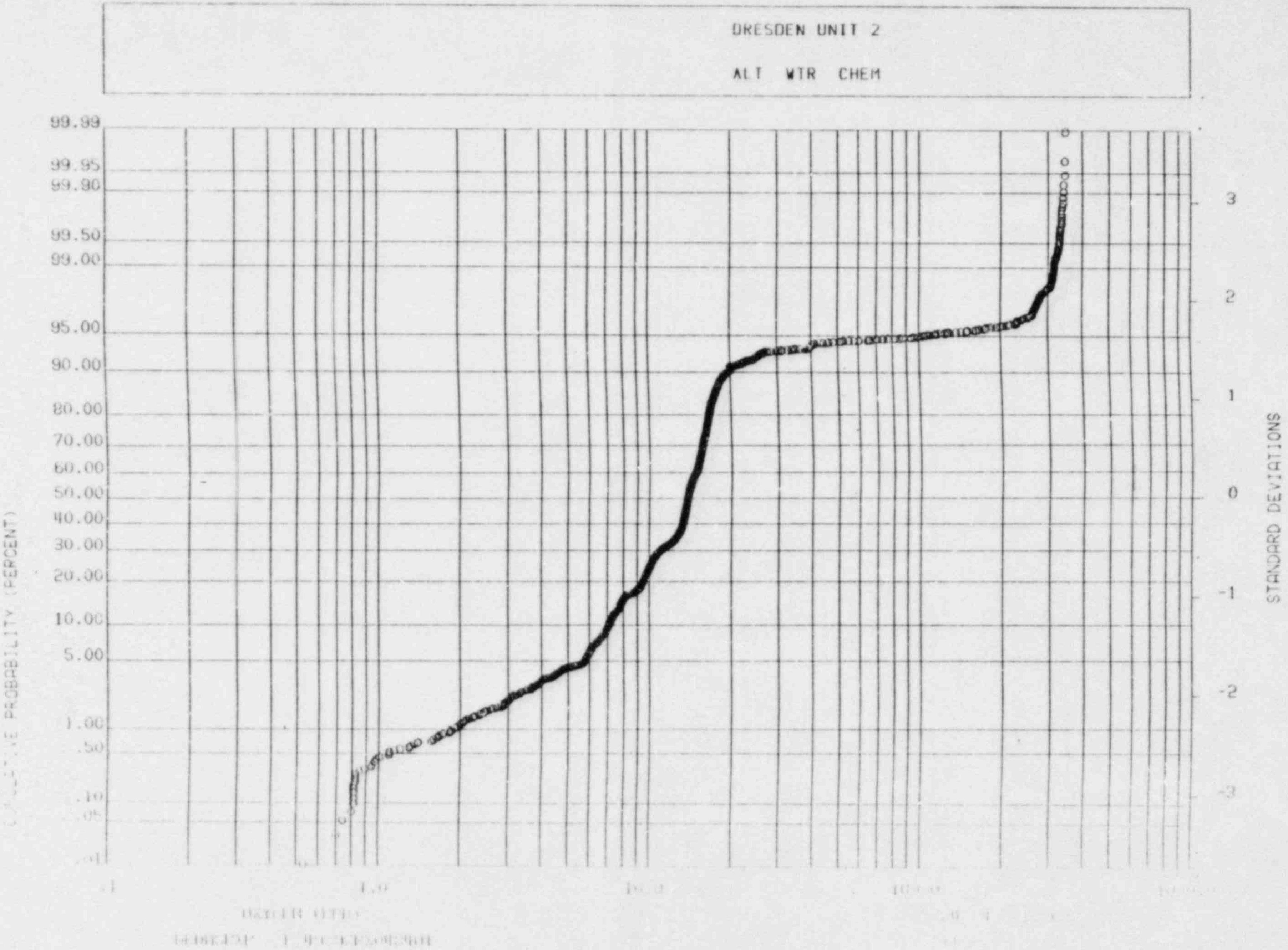


FIGURE 14. APRIL 1984 OXYGEN MEASUREMENTS

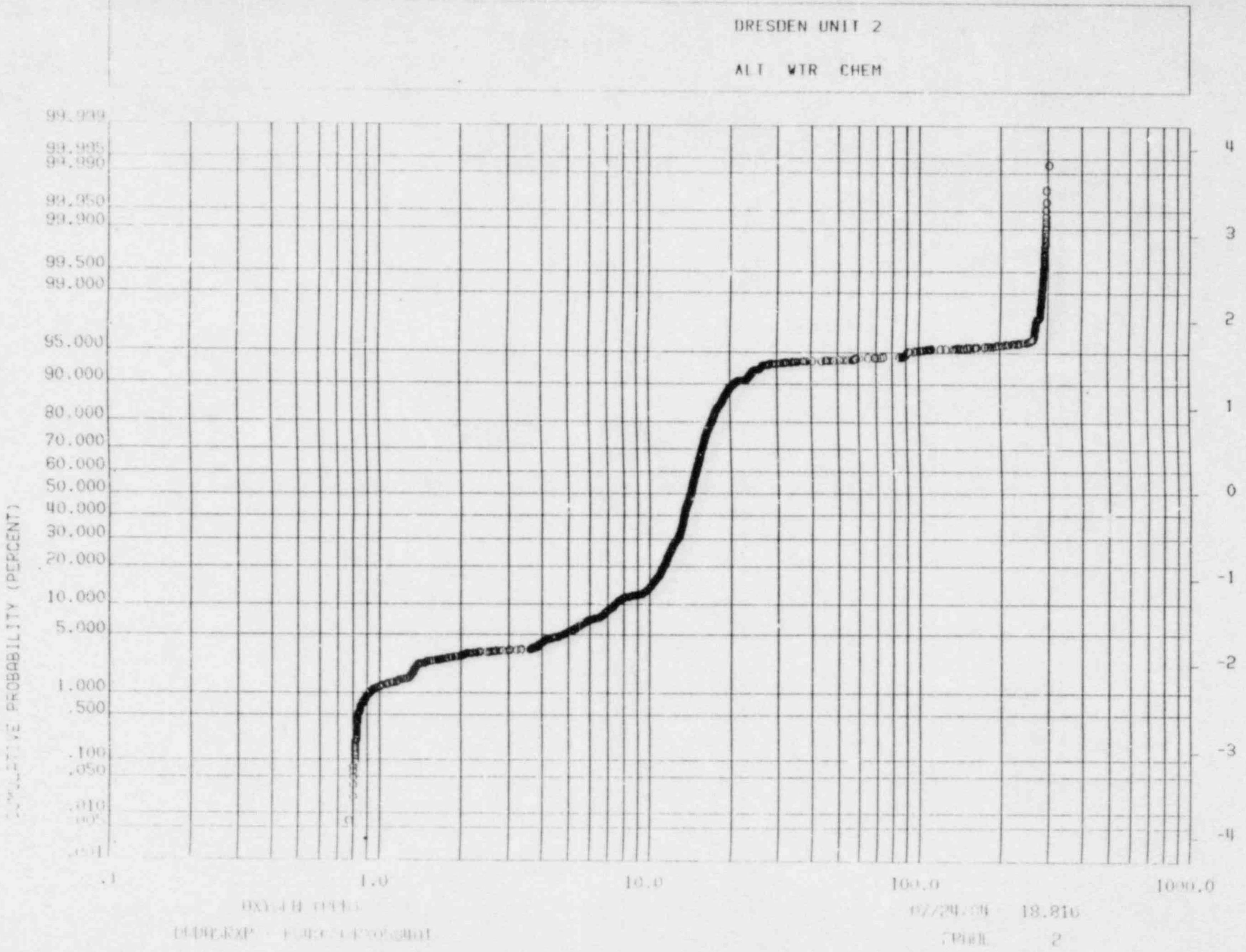


FIGURE 15. MAY 1984 OXYGEN CONCENTRATION

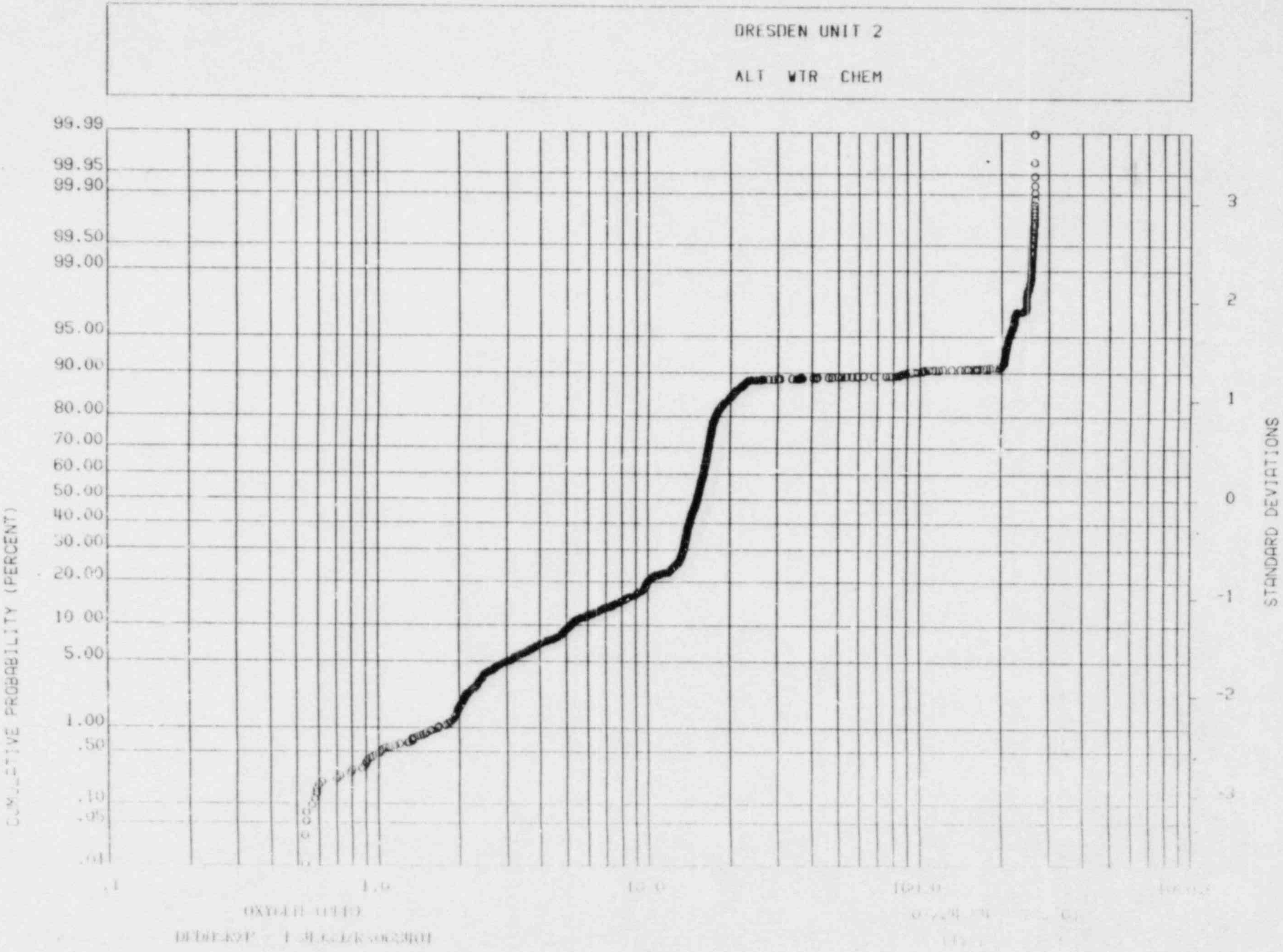


FIGURE 16. JUNE 1984 OXYGEN MEASUREMENTS

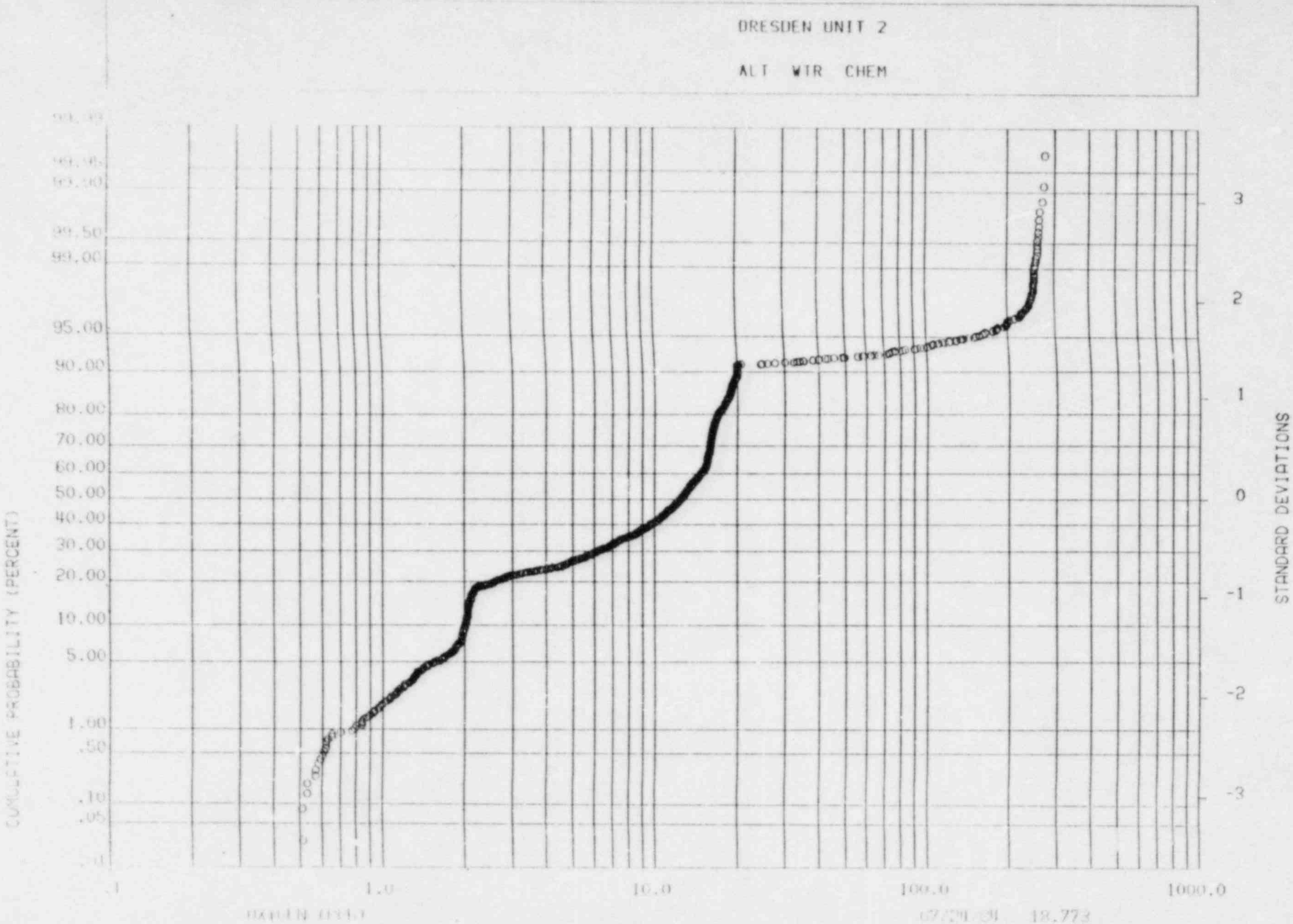


FIGURE 17. JULY 1984 OXYGEN CONCENTRATION

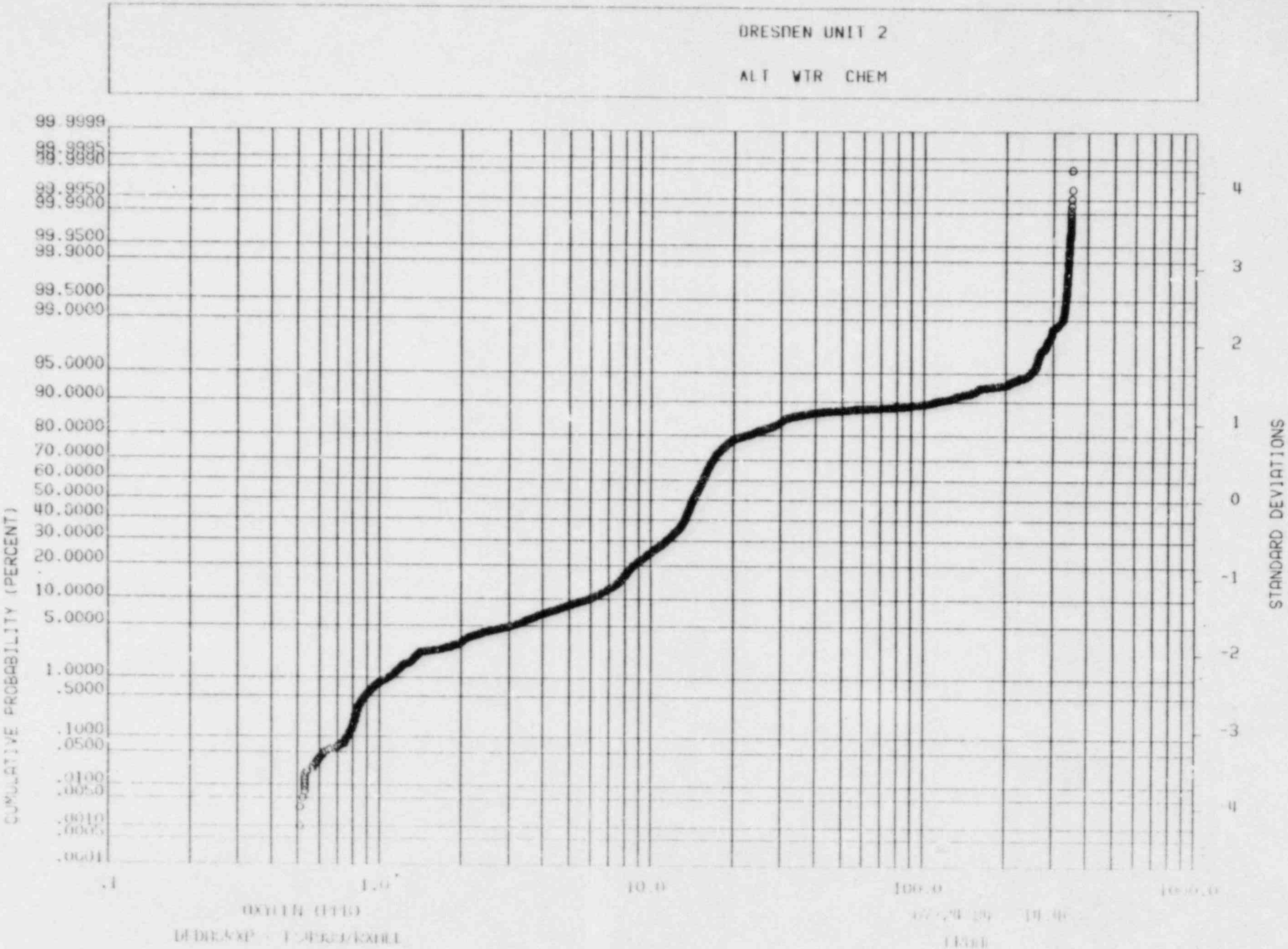


FIGURE 18. PROBABILITY PLOT OF ALL DATA BY PERIOD NOVEMBER,1983 THROUGH JULY 1985

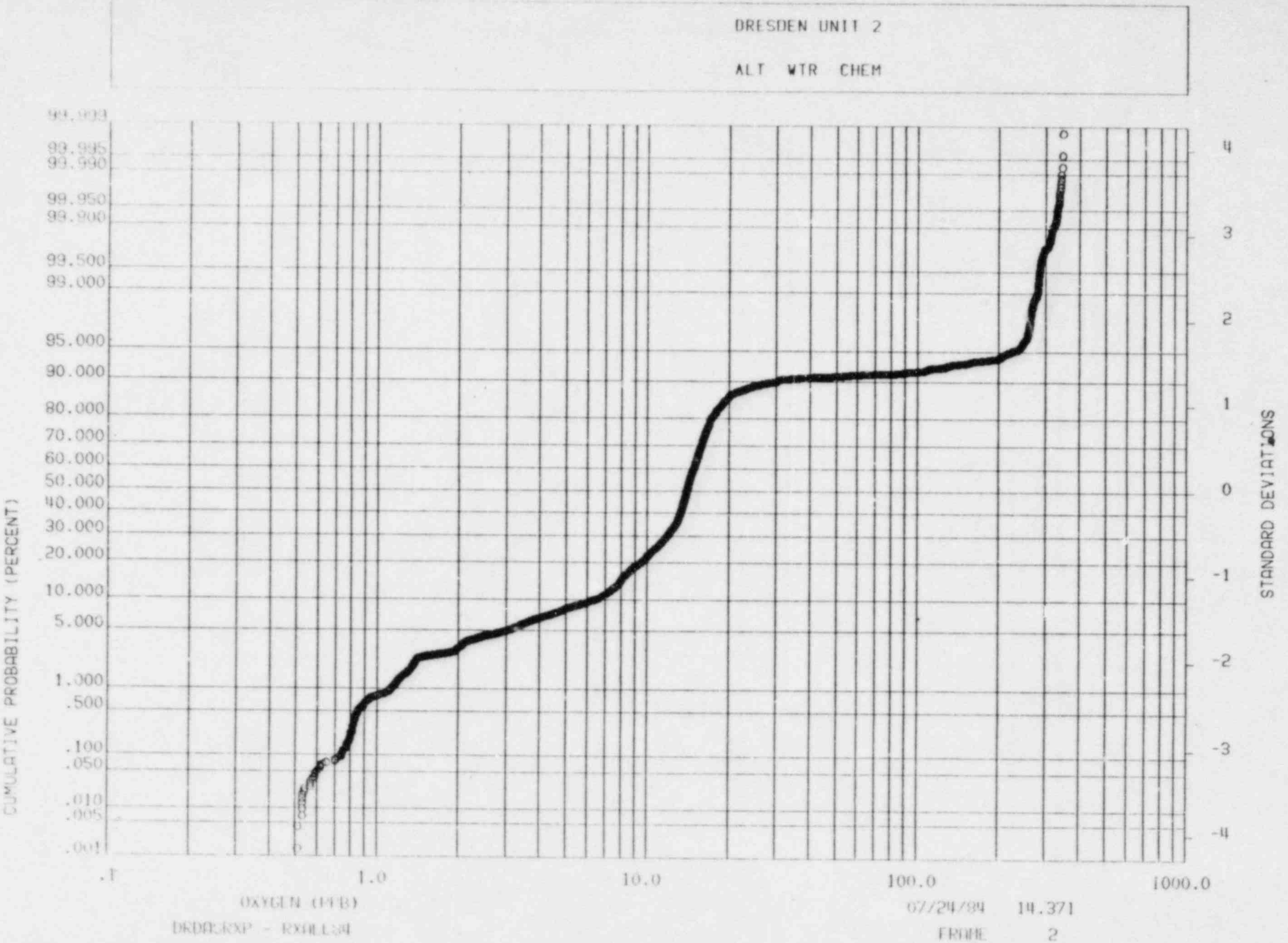


FIGURE 19. PLOT OF ALL OXYGEN CONCENTRATION DATA FOR CALENDAR YEAR 1984

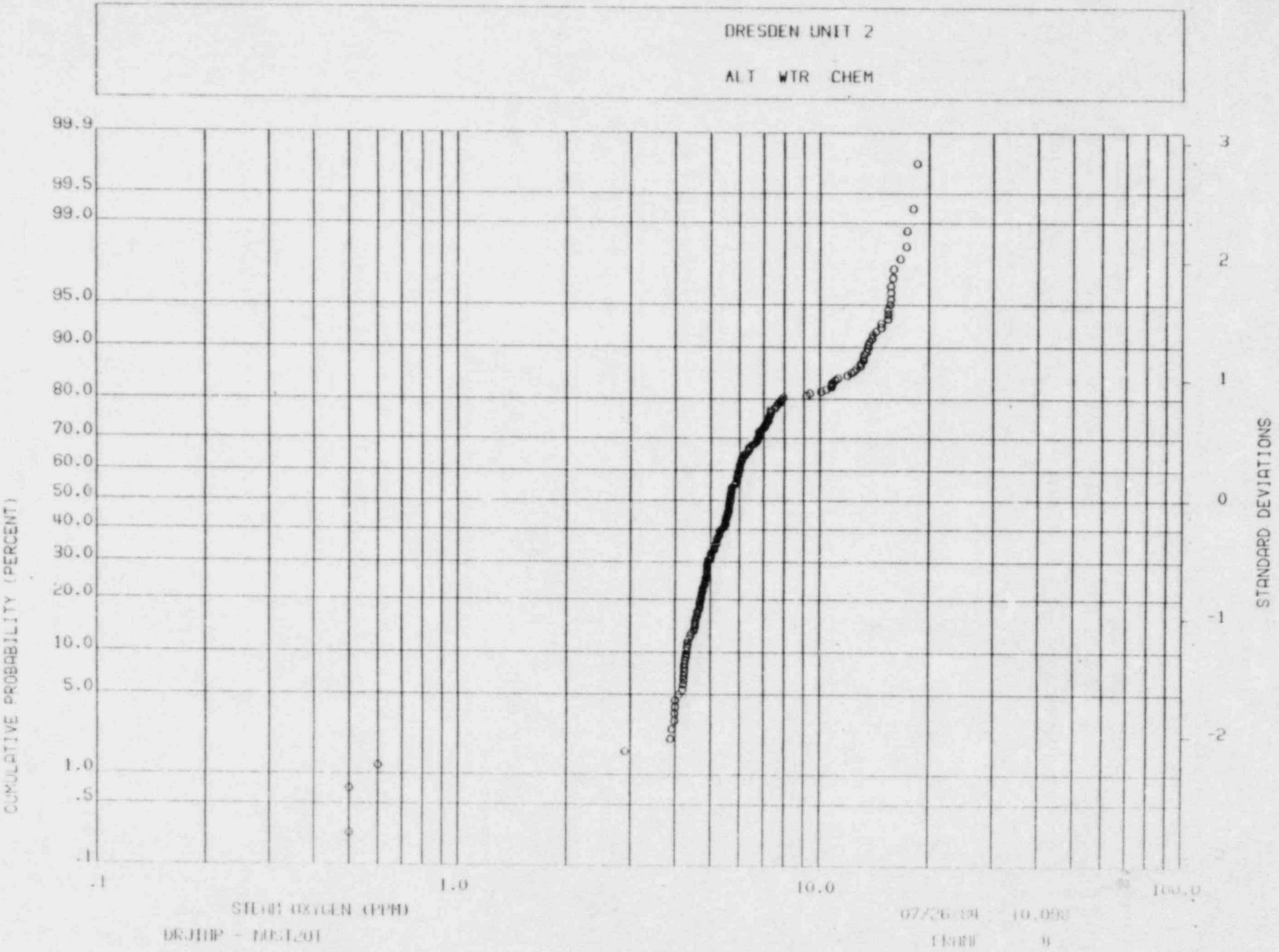


FIGURE 20. MAIN STEAM OXYGEN CONCENTRATION FOR THE PERIOD OF JULY, 1983 TO JULY, 1984

5. HWC IMPACT ON OPERATING DOSE RATES AND OCCUPATIONAL EXPOSURE

5.1 ENVIRONMENTAL DOSE RATE MEASUREMENTS AS A FUNCTION OF HYDROGEN ADDITION

One of the critical effects of the Hydrogen Water Chemistry (HWC) program is the effect on environmental dose rates and personnel exposure. The increase of volatile N-16 was expected with HWC, resulting in a significant increase in the steam lines dose rate. During the May 1982 HWC test at Dresden-2,[1] steam line radiation was monitored (Figure 1) and a single point was measured near the reactor building for environmental dose. Further studies were needed to estimate the effect of this increase on property line yearly dose rate. During a period of 12 months, starting in May 1983, Applied Process Technology (APT) under contract to EPRI made environmental dose rate measurements at 30 locations. The net dose rates (with H_2-without H_2) found by APT are shown in Figure 2 [2,3] as a function of distance and direction from the Dresden-2 turbine.

A series of measurements were performed by General Electric during early June 1984, to determine the levels with and without Hydrogen addition, and ten days later, measurements of the "background" with both operational plants in shutdown as an independent check. Twenty-four locations were measured under all three conditions and varied in distance from the D-2 turbine from 400 to 2800 ft. During these tests, the Dresden-3 unit was shutdown and there were no contributions of N-16 and C-15 to the dose measured. The other activities from radioactive waste and long-lived activation and fission products, however, were still present and contributed to the dose rate. The background rate represented the combined man made, cosmic, and terrestrial radiation.

The primary measurement instrument was a Reuter-Stokes Model RSS-111 area monitoring system.[4] The RSS-111 consists of two modules: [1] The high pressure ionization chamber, and [2] a readout/power supply system. It is completely battery operated, and thus, completely portable. It has an upper limit of 500 uR/h and a sensitivity of 20 mV/uR/h. The readout is a strip chart recorder with auto ranging 0-50 and 0-500 uR/h and a digital light emitting diode (LED) readout. A single point is plotted every two seconds and the chart speed is 4 in./hr., allowing recording of individual readings. The actual measurements of ionization chamber current are made with a sensitive electrometer (20 mV/uR/h). The ionization chamber is a spherical stainless steel shell filled with ultra pure argon and provides a flat response from about 0.5 meV to greater than 8 meV.

The measurements were taken over a single day for each of the conditions, both with and without hydrogen (hydrogen flow rate of 50 scfm) at 95 to 100% full reactor power. The shutdown measurement was taken 25 hrs. after the actual shutdown. These 24 measurements agreed with the data shown in Figure 2 to an outstanding degree. The few anomolies are due to movement of sources which affect the gross readings on a single day and subsequently the net values.

The effect of HWC on the ALARA (man Rem) of Dresden-2 is an important consideration. The reported total incremental dose rate (man-Rem/yr) from HWC will result in an increase of 10 man-Rem/year.[3] The man-Rem/yr will be a small increase when compared to average normal BWR exposures of 1000 man-Rem (2300 man-Rem, Dresden 1981). Conversely, HWC could offset the need for a piping replacement effort, which is known to cost in the range of 1200-2400 man-Rem. The small potential annual increase thus is very ALARA effective when compared to the known impact of IGSCC on plant operations.

The dose rate surveys and gamma scan at Dresden-2 have been measured at five different locations, all on the 517 ft level of the drywell. The dose rates on the surface of the pipe and the gamma scans at distance from the pipe are measured at exactly the same location each time. The dose rates measured are shown in Figure 3 as a function of effective full power years (EFPY). The gamma scan measureements are shown in Figure 4.

5.2 RECIRCULATION LOOP PIPING DOSE RATES

Over the last ten years, General Electric has evaluated the dose rate increase with operating time for a number of BWR units. Basically, this study was undertaken to provide an understanding of radiation buildup and control. Using this data as a base, calid comparisons can be made within the BWR community, and predictions of radiation buildup can be made. In evaluating the effect of HWC on radiation buildup in the recirculation loops, these developed measurement techniques were utilized. A gamma survey and scan were performed in March 1983, prior to the long term use of hydrogen. During short outages (24 hrs) of Dresden-2 in November 1983, and again in June 1984, gamma surveys of the recirculation loop piping in the drywell were made at that time.

The dose rate surveys are taken with two different instruments, one a portable ionization chamber, Eberline R05A, and a shielded directional probe, Eberline HP220 probe coupled with a digital readout, normally referred to as Directional Probe Gamma Survey Measurement (DPGSM). The R05A measurement results in a measurement of the dose rate at a point unshielded and affected by surrounding sources of radiation. The DPGSM results in a dose rate at the pipe surface and shielded from extraneous sources. Both of the measurements of dose are obtained at the surface of the insulation or pipe (i.e., contact readings). The dose rate instrumentation is calibrated before and after each test with a source whose calibration is traceable to NBS. The measurements are corrected by any nonlinearities and bias found in the standardization.

The gamma scans are performed with a highly shielded and collimated IGE solid state detector, coupled with a portable battery operated multichannel analyzer. The total system has been extensively calibrated to allow the conversion of count rate in a gamma peak to microcuries per square centimeter on piping. The conversion allows correction for the pipe thickness, diameter, and counting geometry. A standard source is used to check the calibration before, during, and after each series of gamma scans.

The dose rate surveys and gamma scan at Dresden-2 have been measured at five different locations, all on the 517 ft level of the drywell. The dose rates on the surface of the pipe and the gamma scans at distance from the pipe are measured at exactly the same location each time. The dose rates measured are shown in Figure 3 as a function of effective full power years (EFPY). The gamma scan measurements are shown in Figure 4.

The increases in dose rate and Co-60 activity levels with time are not higher than would be expected in a non-hydrogen operating BWR. The pre-hydrogen levels in Dresden-2 were lower than most domestic BWRs and at longer exposure than most. The slope of the increase from initial startup to the prehydrogen was less than 40 mR/h/EFPY. The increase in levels between March 1983 and June 1984 have a slope of 38 mR/h/EFPY and are certainly within the statistical variation of the measurements. The June 1984 measurements included a section of new pipe which had been replaced in the reactor water cleanup system heat exchanger system and a measurement of the pipe (not replaced) adjacent to it. The measured dose rates with the DPGSM showed 435 mR/h on the new pipe and 531 mR/h on the old pipe. The old pipe had seen an exposure of 8.64 EFPY and the new pipe 1.06 EFPY. This result was expected since with HWC conditions specific activity of Co-60 (uCi/gm) had increased by a factor of 3-4 and the corrosion film produced is thinner by a factor of 4-5, resulting in counteracting effects. It is concluded that HWC does not increase dose rates and/or activity levels above their normal pattern.

REFERENCES

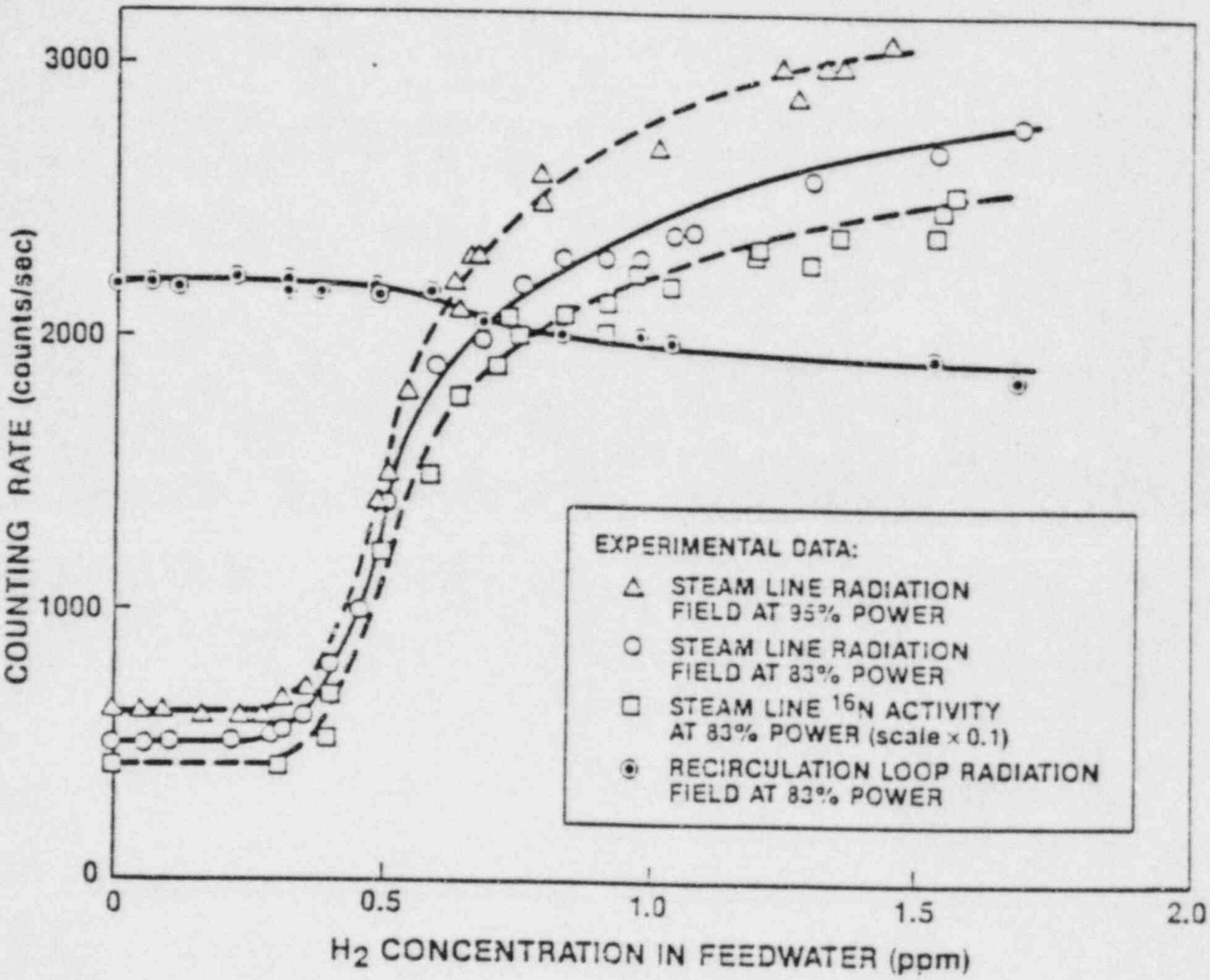
1. "Oxygen Suppression in Boiling Water Reactors - Phase 2, Final Report," NEDC-23856-7.

2. JTA Roberts, R. L. Jones, M. Naughton, "Mitigation of BWR Pipe Cracking Through Chemistry Changes," American Power Converence, Chicago, Ill., April 1984.

3. E. L. Burley, "BWR Hydrogen Water Chemistry Radiological Monitoring," EPRI Hydrogen Addition Project Review, Dresden Site, April 25, 1984.

4. W. M. Lowder. D. D. Raft, G. DeP Burke, "Determination of N-16 gamma Radiation Fields at BWR Nuclear Power Status," HASL-305. May 1976.

FIGURE 1



STEAM LINE RADIATION

FIGURE 2

NET HWC CONTRIBUTION TO DRESDEN ENVIRONS DOSE RATES (μR/H)

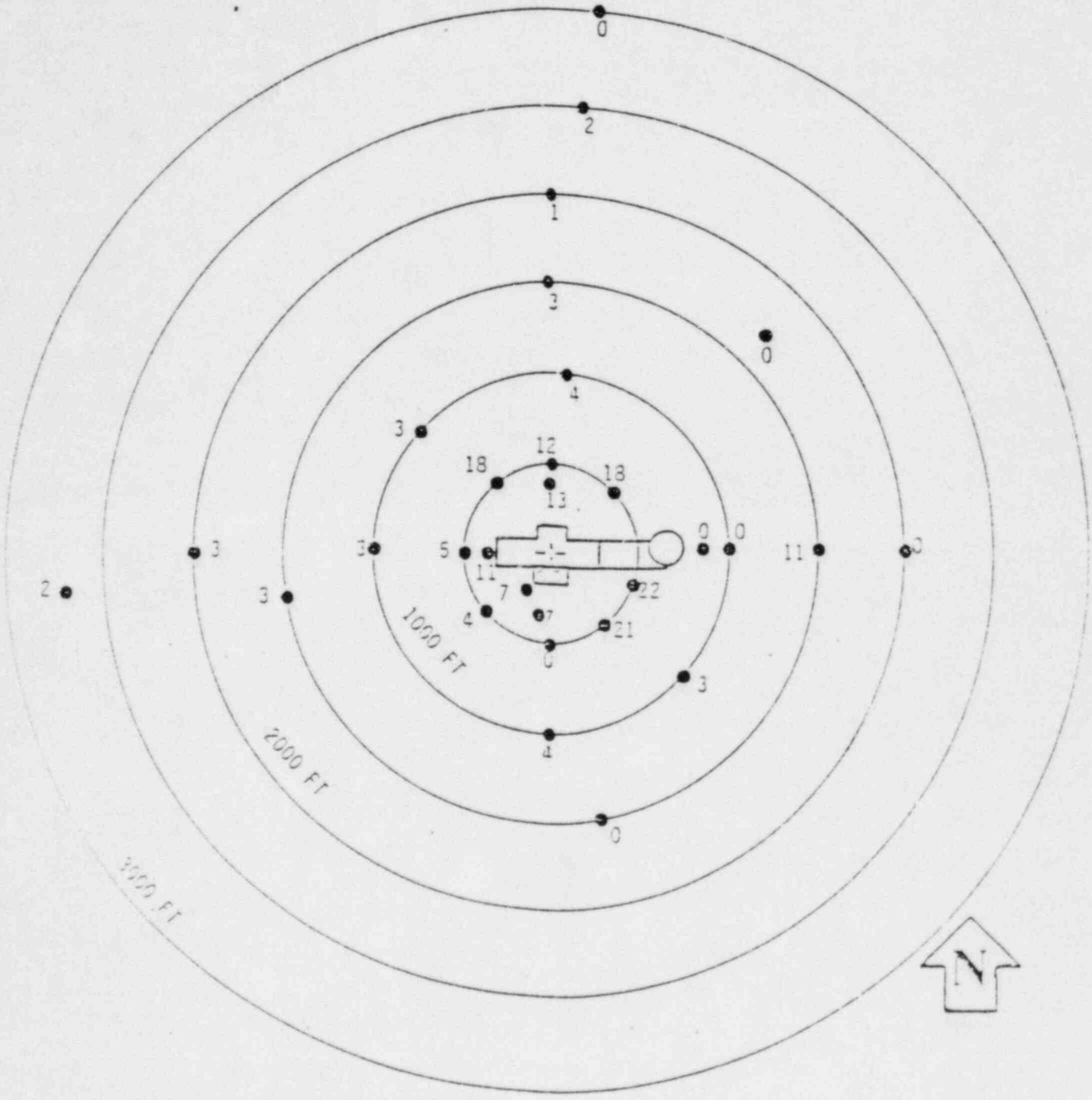


FIGURE 3

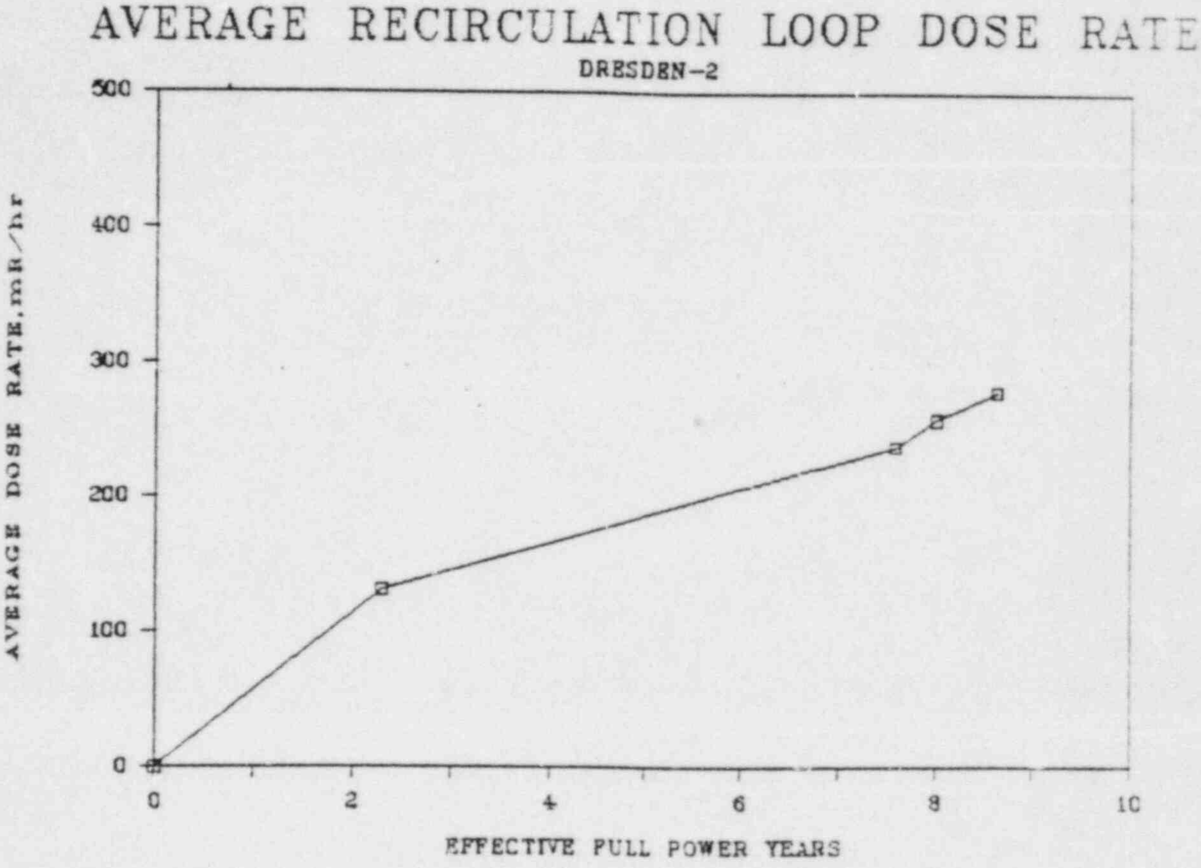
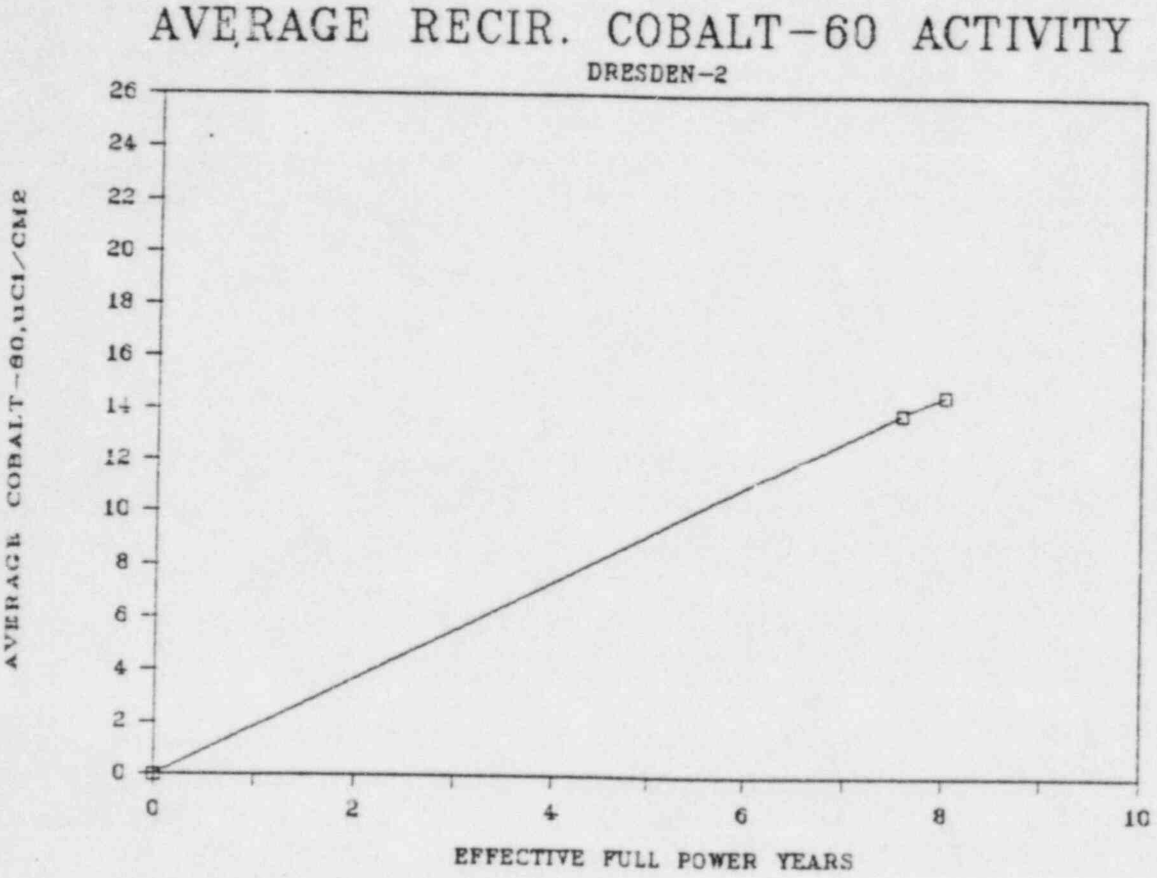

AVERAGE RECIRCULATION LOOP DOSE RATE
DRESDEN-2
AVERAGE DOSE RATE, mR/hr
0
100
200
300
400
500
0
2
4
6
8
10
EFFECTIVE FULL POWER YEARS

FIGURE 4


AVERAGE RECIR. COBALT-60 ACTIVITY
DRESDEN-2
AVERAGE COBALT-60,uCi/CM2
0
2
4
6
8
10
12
14
16
18
20
22
24
26
EFFECTIVE FULL POWER YEARS
0
2
4
6
8
10

6.0 . FUELS PERFORMANCE AND SURVEILLANCE PROGRAM

6.1 DRESDEN-2 FUEL PERFORMANCE

Fission product release measurements are used to estimate fuel failures in a boiling water reactor during plant operation. Station chemists routinely measure six noble gas isotopes (Xe-133, Xe-135, Xe-138, Kr-85m, Kr-87, and Kr-88) and five radioiodine isotopes (I-131, I-132, I-133, I-134, and I-135) being released from the nuclear core. A recent set of measurements made at Dresden 2 are shown in Figure 1. The release rate has been normalized by dividing the release rate of each of the six noble gas isotopes and five radioiodine isotopes by its fission yield and decay constant. Since the normalized release for these isotopes is nearly the same, we can confidently state that there is no failed fuel in the core. This pattern was observed in essentially all of the samples taken during a 57 week period of Dresden Fuel Cycle 9. It is characteristic of a recoil fission source estimated to be 2.6 E 12 fissions/sec supporting the generation and release of the measured fission products.

Recoil release is observed from uranium impurities in the fuel cladding and plateout of fissionable material on the surfaces of the core. A 2 ppm natural uranium impurity level in the cladding will yield about 30 microcuries/sec of noble gases (sum of six isotopes). This is the order of magnitude observed in new reactor cores.

Figure 2 shows the noble gas release (sum of six isotopes) during Fuel Cycle 9 at Dresden 2. A least squares fit of the data suggest that the noble gas release was about 6500 microcuries/sec at the beginning of the fuel cycle and has been decreasing. Recent values below 4500 microcuries/sec suggest that the fissionable material source is slowly decreasing by either burnup or removal by the reactor water cleanup system.

We can conclude that the recoil pattern observed during the period April, 1983 to June. 1984, as well as the decreasing noble gas release, provides evidence that no failed fuel exists in the Dresden 2 core. The fission products being produced and released are from a small amount of fissionable material plated-out on the surface of the core from failed fuel present in prior fuel cycles.

6.1 DRESDEN 2 FUEL PERFORMANCE

Fission product release measurements are used to estimate fuel failures in a Boiling Water Reactor during plant operation. Station chemists routinely measure six noble gas isotopes (Xe-133, Xe-135, Xe-138, Kr-85m, Kr-87, and I-135) being released from the nuclear core. A recent set of measurements made at Dresden 2 is shown in Figure 1. The release rate has been normalized by dividing the release rate of each of the six noble gas isotopes and five radioiodine isotopes by its fission yield and decay constant. Since the normalized release for these isotopes is nearly the same, we can confidently state that there is no failed fuel in the core. This pattern was observed in essentially all of the samples taken during a 57 week period of Dresden Fuel Cycle 9. It is characteristic of a recoil fission source estimated to be 2.6 E 12 fissions/sec supporting the generation and release of the measured fission products.

Recoil release is observed from uranium impurities in the fuel cladding and plateout of fissionable material on the surfaces of the core. A 2 ppm natural uranium impurity level in the cladding will yield about 30 microcuries/sec of noble gases (sum of six isotopes). This is the order of magnitude observed in new reactor cores.

Figure 2 shows the noble gas release (sum of six isotopes) during Fuel Cycle 9 at Dresden 2. At least squares fit of the data suggest that the noble gas release was about 6500 microcuries/sec at the beginning of the fuel cycle and has been decreasing. Recent values below 4500 microcuries/sec suggest that the fissionable material source is slowly decreasing by either burnup or removal by the reactor water cleanup system.

We can conclude that the recoil pattern observed during the period April, 1983 to June, 1984, as well as the decreasing noble gas release, provides evidence that no failed fuel exists in the Dresden 2 core. The fission products being produced and released are from a small amount of fissionable material plated-out on the surface of the core from failed fuel present in prior fuel cycles.

6.2 FUEL SURVEILLANCE PROGRAM

Hydrogen additions to the water of Biling Water Reactors (BWRs) creates a water chemistry condition which is outside the experience base of either BWRs or Pressurized Water Reactors (PWRs). Therefore, it is prudent to ascertain the effects of the altered water chemistry on fuel performance and surveillance program has been established at Dresden-2. This General Electric/EPRI program is described below.

Four bundles (LTAs) of carefully characterized fuel components have been inserted at the beginning of the first cycle of hydrogen addition. Zircaloys with a known, precharacterized range of corrosion behavior representative of the range usually found with cladding batches used in BWR fuel fabrication have been selected for these bundles. The preirradiation characterization report (Subtask 1.1) will qualitatively specify the expected corrosion behaviors of the rods and spacers constituting the LTAs. In addition, discharged fuel bundles having been exposed to various combinations of normal BWR water chemistry and hydrogen water chemistry cycles are also included in the test matrix.

A combination of site and hot cell examinations will provide required information on corrosion and hydriding characteristics of Zircaloy-2 and -4 fuel bundle components, and on crud deposition characteristics of the test reactor plant. Components examined will be urania fuel rods, gadolinia-urania fuel rods, spacers, and water rods. Table 1 outlines the proposed fuel surveillance program.

As shown in Table 1, no examinations have been conducted prior to the first cycle of hydrogen addition; however, one bundle of three-cycle discharged fuel will be identified for future examination. After the first cycle of hydrogen water chemistry conditions,e xaminations will be conducted on this bundle (designated as 3/0, i.e., 3 cycles of normal BWR water chemistry and 0 cycle of hydrogen water chemistry), a 2/1 discharged bundle, and a 0/1 LTA bundle. Poolside examination may identify gross changes in the corrosion behavior due to hydrogen water chemistry, but Zircaloy hydriding infomration will not e available until completion of the first hot cell exam in mid-1985 (refueling outages are assumed to be on an 18-month cycle). After cycle 2 another LTA bundle (0/2) and another discharged bundle (1/2) will be examined. After cycle 3, a third LTA bundle (0/3) will be available for examination, such work is considered optional at this time.

TABLE 1. Fuel Surveillance

Outage	BWR/HWC Cycles	Site Examination	Hot Cell Exam	Comments
0	--	None	None	
1	3/0	1 Bundle Oxide Visual 12 U, 4 Gd Crud - 4 U, 2 Gd	2 U, 1 Gd	Discharge in Cycle 0
	2/1	1 Bundle Oxide Visual 12 U, 4 Gd Crud - 4 U, 2 Gd	2 U, 1 Gd	Discharge in Cycle 1
	0/1 (LTA-A)	Bundle Oxide Visual 8 U, 4 Gd Crud - 4 U, 2 Gd	2 U, 1 Gd 1 H_2O Rod 4 Spacers	Replacement fuel required
2	1/2	Same as 3/0 ----------------------		Discharge in Cycle 2
	0/2 (LTA-B)	Same as 0/1 LTA -----------------		Replacement fuel required

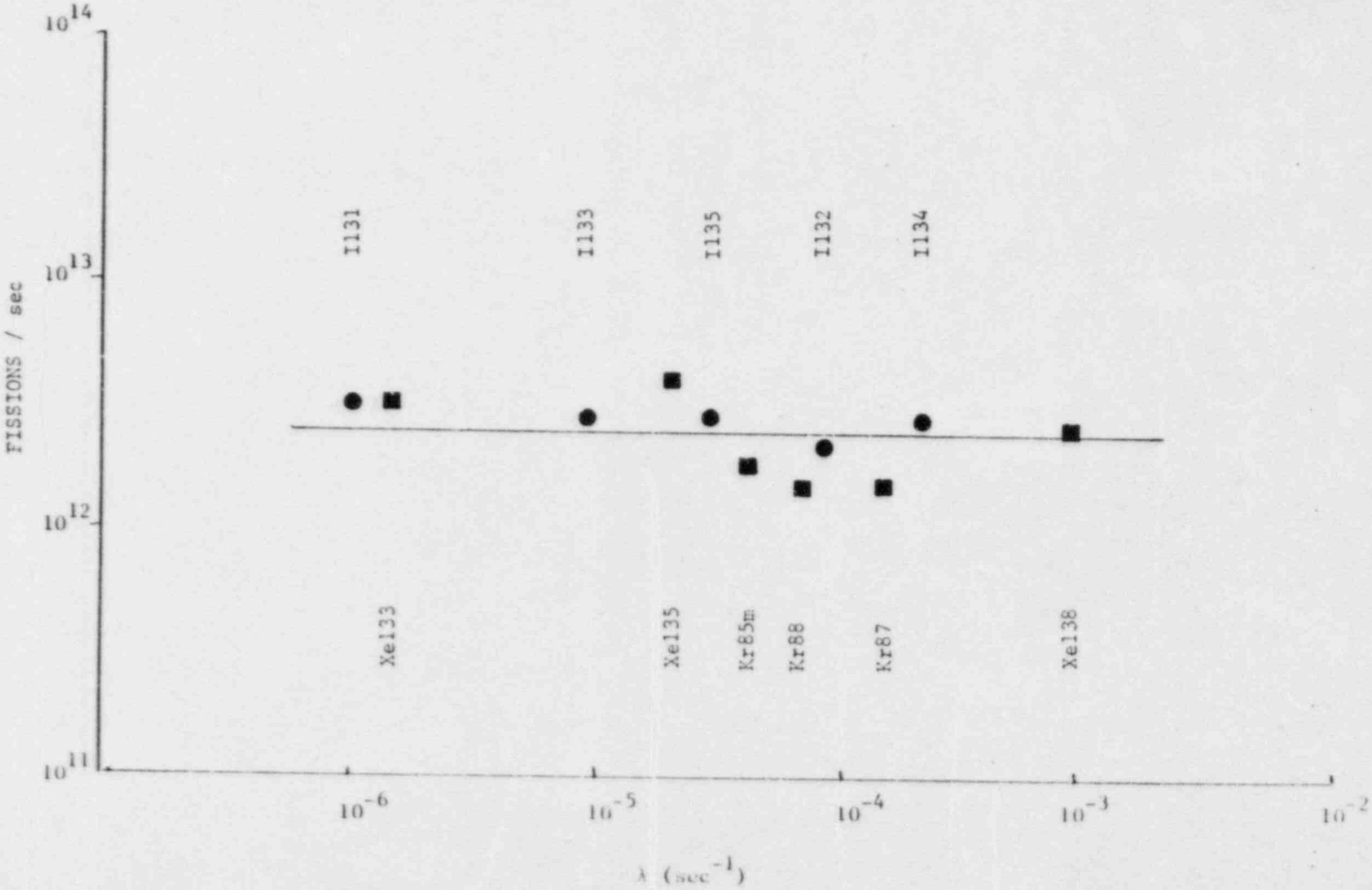


FIGURE 1. TYPICAL FISSION GAS VALUES DURING HYDROGEN WATER CHEMISTRY PROGRAM (TAKEN 6/12/84)

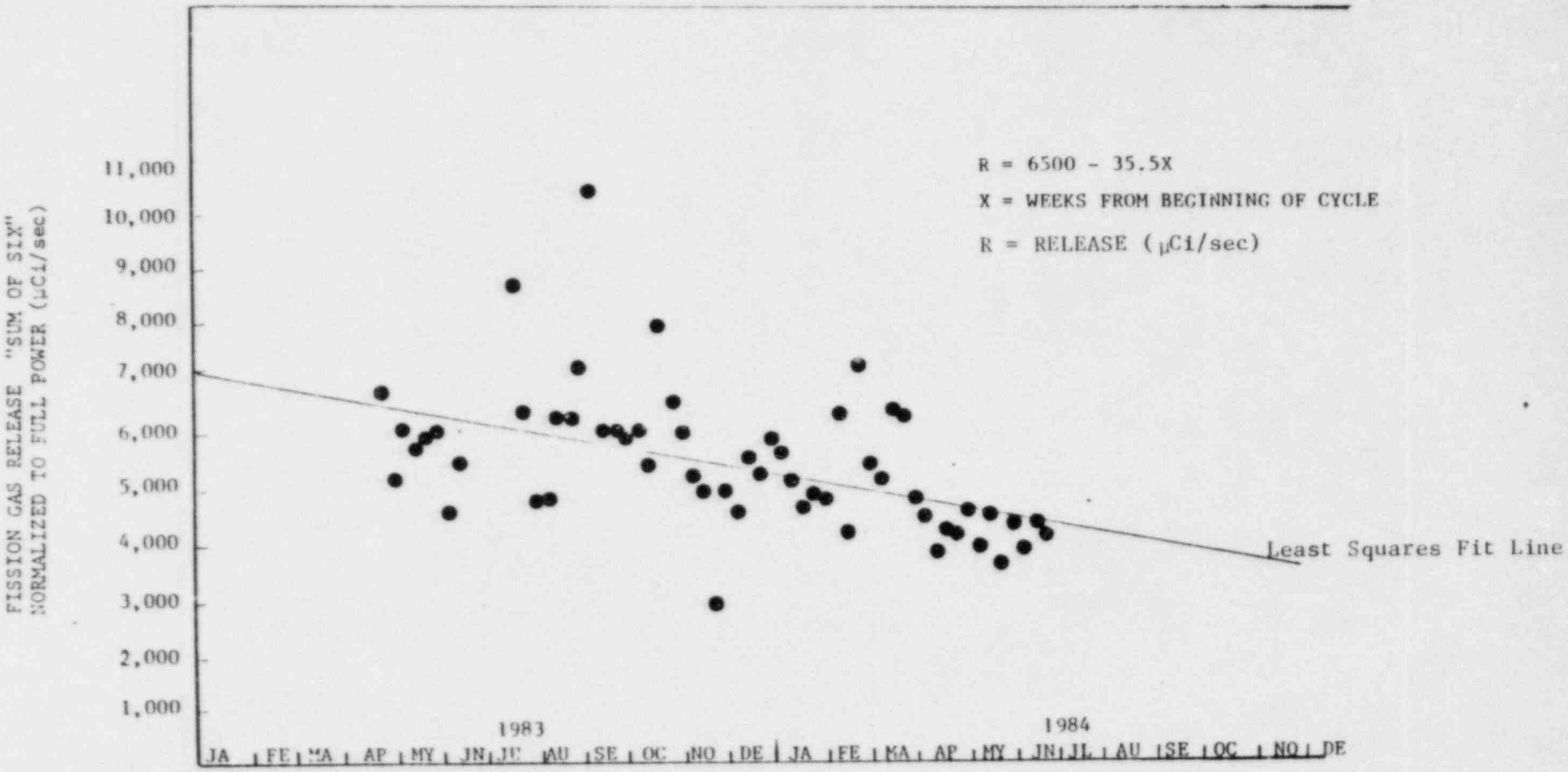


FIGURE 2. "SUM OF SIX" FISSION GAS RELEASE VALUES DURING THE HYDROGEN WATER CHEMISTRY PROGRAM

APPENDIX A

TECHNICAL BASIS FOR HYDROGEN WATER CHEMISTRY SPECIFICATION

0.0 EXECUTIVE SUMMARY OF PRINCIPAL FINDINGS

0.1 The initial work to quantify the HWC water quality specification consisted of investigations designed to clearly demonstrate the improved IGSCC performance of Type 304 stainless steel piping in a hydrogenated BWR environment. Four heats of 10 cm (4-in.) diameter Schedule 80 Type 304 and one heat Type 316 Nuclear Grade stainless steel were evaluated in the nominal BWR operating environment [288°C (550°F) water with 200 ppb dissolved oxygen] and in simulated HWC environment (initially 50-70 and then 20 ppb O_2). The metallurgical condition of the pipes was "as welded."

Two types of pipe tests were used: (1) initiation controlled pipe test (10 tests), and (2) propagation controlled pipe tests (4 tests). The initiation pipe tests investigated piping in the as-welded condition with no intentional pre-existing flaws, while in propagation control tests were intentionally flawed (cracked) in the nominal environment and then subsequently tested further in the hydrogenated environment.

The results of this first series of pipe tests indicated that <u>both</u> low dissolved oxygen and low conductivity are necessary to eliminate IGSCC. It was also determined that IGSCC crack propagation in precracked piping can be terminated if the levels of oxygen and conductivity are low enough. These tests suggested an initial HWC specification of 15 ± 10 ppb dissolved oxygen combined with a conductivity of <0.2 uS/cm.

To supplement this task, three additional pipe tests were performed to determine a factor-of-improvement (FOI) of HWC over the nominal 0.2 ppm oxygen environment. These pipes have demonstrated that HWC (low oxygen and conductivity) prevents crack initiation. For example, in the nominal environment (200 ppb oxygen) cracks will typically initiate in approximately 300 hours. However, in HWC no cracks have been identified after approximately 7500 hours, indicating a FOI of 25.

Two additional pipes, each precracked in 200 ppb oxygenated water for 340 hours, were exposed under constant load in the nominal and HWC environments to determine the effects of cycling the stress on pipe performance. The pipe exposed to the nominal environment failed after approximately 1300 hours of exposure, while the other precracked HWC pipe did not fail after an additional 5310 hours of exposure.

0.2 Crack Propagation Studies

This task, which consisted of three separate subtasks focusing on low cycle carbon steel fatigue tests, fatigue crack growth investigations of stainless, carbon and low alloy steels, and constant load crack growth tests of stainless, carbon and low alloy steel, was characterized by a dual objective: (1) determine the effects of a reduction in the dissolved oxygen level in the coolant as established in the pipe test on the crack propagation rate of key BWR structural materials, and (2) determine the crack arrest and retardation behavior in this specified HWC environment.

The results of these studies indicate that HWC dramatically improves the fatigue crack initiation resistance of carbon steel and retards fatigue and constant load crack growth of stainless, carbon and low alloy steels.

0.3 In-Reactor Tests

Results from the initial Dresden-2 HWC demonstration and subsequent HWC operation plus recent laboratory studies stongly suggest that to obtain the "blanket" protection that HWC seems capable of providing, both the dissolved oxygen and the conductivity of the water must be reduced. The synergism between these two critical variables defines the aggressiveness of the environment. The logic for this synergism is straight-forward: The reduction in dissolved oxygen content reduces the driving force for the necessary cathodic corrosion reaction: $O_2 + 2H_2O + 4e - 4OH$, while the reduction in the conductivity of the electrolyte retards the corrosion rate.

The importance of conductivity was initially indirectly identified during the laboratory pipe tests discussed above where, when the oxygen level and conductivity was reduced from 50-70 ppb to 15 ± 10 ppb and 0.6 ± 0.3 uS/cm to <0.2 uS/cm, respectively, mitigation of IGSCC occurred.

Similar results were identified during the first series of Dresden-2 HWC materials tests where a furnace-sensitized Type 304 stainless steel CERT specimen was characterized by 35% IGSCC of the fracture surface in a reactor environment of 40 ppb O_2 and 0.37 uS/cm conductivity, but had no IGSCC in an improved reactor environment of <20 ppb oxygen and 0.29 uS/cm conductivity. Although oxygen and conductivity were reduced simultaneously in both the laboratory pipe tests and the Dresden-2 CERT test, other laboratory work has isolated these two factors and has provided direct evidence for importance of conductivity on IGSCC, as described below.

CERT tests were performed on weld sensitized Type 304 stainless steel in oxygenated water at 274°C (525°F) with low concentrations of various impurities. The results of this study clearly indicated that the amount of IGSCC in sensitized Type 304 stainless steel is directly related to the specific anion and its concentration/conductivity. For example, at a constant oxygen level of approximately 22 ppb, a solution of Na_2CO_3 with a conductivity of 1.0 uS/cm produced IGSCC; whereas, reducing the conductivity of the same solution to 0.3 uS/cm resulted in ductile failure. Recent results from an ongoing oxygen vs. conductivity CERT study can also be cited as evidence for the efficacy of conductivity.

During the second ECP measurement campaign at Dresden-2 (October 1983 - April 1984), the ECPs of stainless steel was measured for 3330 hours (~139 days). The potentials obtained during this extensive coverage were similar to those measured during the first demonstration campaign. The normal Dresden-2 environment was characterized by an ECP range for Type 304 stainless steel of -100 to -200 mV_{SHE}, while the hydrogenated Dresden-2 environment reduce the Type 304 stainless steel potential to -370 to -460 mV_{SHE}. It appears that during times when HWC is terminated, a "memory" effect occurs in that the potential does not suddenly rise into the range where IGSCC of sensitized Type 304 stainless steel can occur. Instead the potential rises slowly which creates a window of time prior to rising into the cracking potential region. Typically this window is 10 hours.

The 1983-1984 CERT test campaign at Dresden-2 was characterized by a similar set of seven experiments. Four furnace-sensitized Type 304 stainless steel specimens, one furnace-sensitized Type 304 stainless steel specimen (precracked by IGSCC in a 0.2 ppm oxygen water laboratory autoclave and shipped to the site), one SA106 Grade B carbon steel and one SA508 Class II low alloy steel specimens were tested. The results of these CERT tests plus the results of the first campaign and comparable laboratory tests are summarized in Table 1.

Table 1 clearly indicates an excellent correlation between Dresden-2 and laboratory CERT test results. It also clearly shows that HWC provides mitigation of IGSCC in furnace sensitized Type 304 stainless steel even in instances where hydrogen addition has been interrupted. For example, in one CERT study (line No. 6) 396 hours of test time and 45% strain were accumulated with >10% of the test time in oxygenated water (30 hours with no H_2 and 0_2 >200 ppb and 15.5 hours with 0_2 at 25-41 ppb) and no IGSCC was identified. However, in CERT No. 5, a 12 hour continuous test period with the hydrogen injection terminated produced minor IGSCC damage. (This test result is also marred by a thermal overload problem which resulted in extremely high thermal stress.) The precracked furnace-sensitized Type 304 stainless steel specimen (No. 8) (67 hours in 200 ppb 0_2) which was carefully documented prior to in-reactor testing, failed by ductile tearing after 301 hours in Dresden-2. The mechanical parameter of this specimen is similar to non-precracked specimens. It is also important to note that this test included 10 hours >40 ppb oxygen. Finally, no IGSCC was identified in either SA508-2 and SA533-B low alloy steel and SA106-B carbon steel in HWC at Dresden-2 despite interruptions in hydrogen injections.

Crack growth data versus time and environment on precracked furnace-sensitized Type 304 stainless steel is being obtained at Dresden-2 using the reversing DC potential drop technique as developed by GE Corporate Research and Development. The specimen was precracked in San Jose in the nominal 200 ppb O_2 and then transported to Dresden-2 for testing. The K_I level for the specimen bounds the crack previously identified in Dresden-2 safe-end at 27.5 MPa /m (25 ksi /in). To supplement this program, bolt loaded WOL specimens (one each) of Alloy 600 and unclad SA508 Cl. II low alloy steel have also been insertd into the autoclave.

Figure 1 presents the early DC potential drop crack growth data of the precracked furnace-sensitized Type 304 stainless steel specimen. Although the data is preliminary and is clouded by a reactor scram which occurred approximately 120 hours into the test and some other interruptions in hydrogen injection, no significant crack growth has occurred on the specimen. This preliminary result verifies the result of the Dresden-2 precracked CERT test discussed above and the results of the mid-cycle in-service inspection (ISI) as presented in Table 2.

This mid-cycle ISI was performed as required by the NRC t_ verify the mitigation of IGSCC growth by HWC. The inspection was performed on November 12, 1983, after approximately 5.5 months of operation with hydrogen injection. The results presented in Table 2 indicate that despite interruptions in hydrogen injection, no crack growth was detected by ultrasonic testing.

prerequisities for IGSCC [a sensitized microstructure (chromium depletion at the grain boundaries) and a tensile stress above the yield stress] also are present. A variety of IGSCC remedies has been developed and qualified which address the sensitization and tensile stress aspects of stress corrosion cracking, including Nuclear Grade Type 316 and 304 stainless steels, solution heat treatment (SHT), corrosion-resistant cladding (CRC), heat sink welding (HSW) and induction heating stress improvement (IHSI). It should also be possible to suppress IGSCC by reducing the electrochemical driving force for IGSCC, i.e., by modifying the BWR coolant environment.

The demonstration of an IGSCC remedy based on modifying the chemistry of the BWR coolant is the objective of this materials program. The basic concept is to reduce the aggressiveness of the BWR environment by adding hydrogen gas to the feedwater to reduce the dissolved oxygen concentration in the reactor water and reduce the coolant conductivity to a low value by improved operational practices. This approach appears to have the potential for "blanket" protection of all types of BWR structural materials during power operation of the plant and may arrest the growth of incipient cracks.

To accomplish the project objective of evaluating and quantifying the beneficial effects of oxygen suppression through hydrogen addition, numerous laboratory and Dresden-2 in-reactor testing techniques have been used to study a broad range of BWR structural materials and corrosion phenomena. The results of these laboratory materials programs and Dresden-2 operational results which established the hydrogen water chemistry (HWC) specification are the subject of this chapter. Appendix A describes the detailed results of the HWC materials program.

Table 1

Results of Dresden-2 and Laboratory HWC CERT Tests

	Material	Test Location	O_2 (ppb)	K[1] (uS/cm)	Time To Failure(h)	Time Off HWC(h)	Elongation %	Result
1)	FS[2] T-304	D-2	268	0.29	108	0	12	70% IGSCC
2)	FS T-304	D-2	40	0.37	143	2	20	35% IGSCC
3)	FS T-304	D-2	<20	0.29	>297	4	38	DF[3]
4)	FS T-304	D-2	5-20	0.19	208[4]	5	NM[5]	DF
5)	FS T-304	D-2	5-23	0.17	181	15	NM	Minor IGSCC along gauge
6)	FS T-304	D-2	3-30	0.13	396	36	45	DF
7)	FS T-304	D-2	7-19	0.09	400	25	46	DF
8)	FS T-304PC[6]	D-2	12-20	0.09	301[7]	7	40	No IGSCC Extension
9)	FS T-304	VNC[8]	195	<0.1	156	NA[9]	17	85% IGSCC
10)	FS T-304	VNC	15	<0.1	262	0	NA	DF
11)	SA 533B	D-2	150-280	0.29	37[10]	NA	12	40% TGSCC
12)	SA 533B	D-2	5-20	0.29	63	0	24	DF
13)	SA 533B	VNC	200	<0.1	43	NA	11	40% TGSCC
14)	SA 533B	VNC	12	<0.1	60	0	22	DF
15)	SA 508-2	D-2	12-18	0.08	52[11]	0	NM	DF
16)	SA 508-2[12]	VNC	50	<1	44	0	29	DF
17)	SA 106B	D-2	8-14	0.12	94	2	NA	DF
18)	SA 106B	VNC	50	<1	40	0	29	DF

1) K = Conductivity
2) FS = Furnace Sensitized 621°C (1150°F)/24 hr
3) DF = Ductile Fracture
4) Thermal Overload Ended Test
5) NM = Not Measured to Date
6) PC = Precracked in 200 ppb O_2
7) Plus 67 Hours Precracking (368 hr total)
8) VNC = Vallecitos Nuclear Center
9) Not Applicable. i.e., not a HWC Test
10) Extension rate was 3 mils/h for SA 533, SA 508-2, SA 106B and 1 mil/h for Type 304 Stainless Steel
11) Motor Failure, Specimen Fractured Manually
12) Creviced

Table 2.

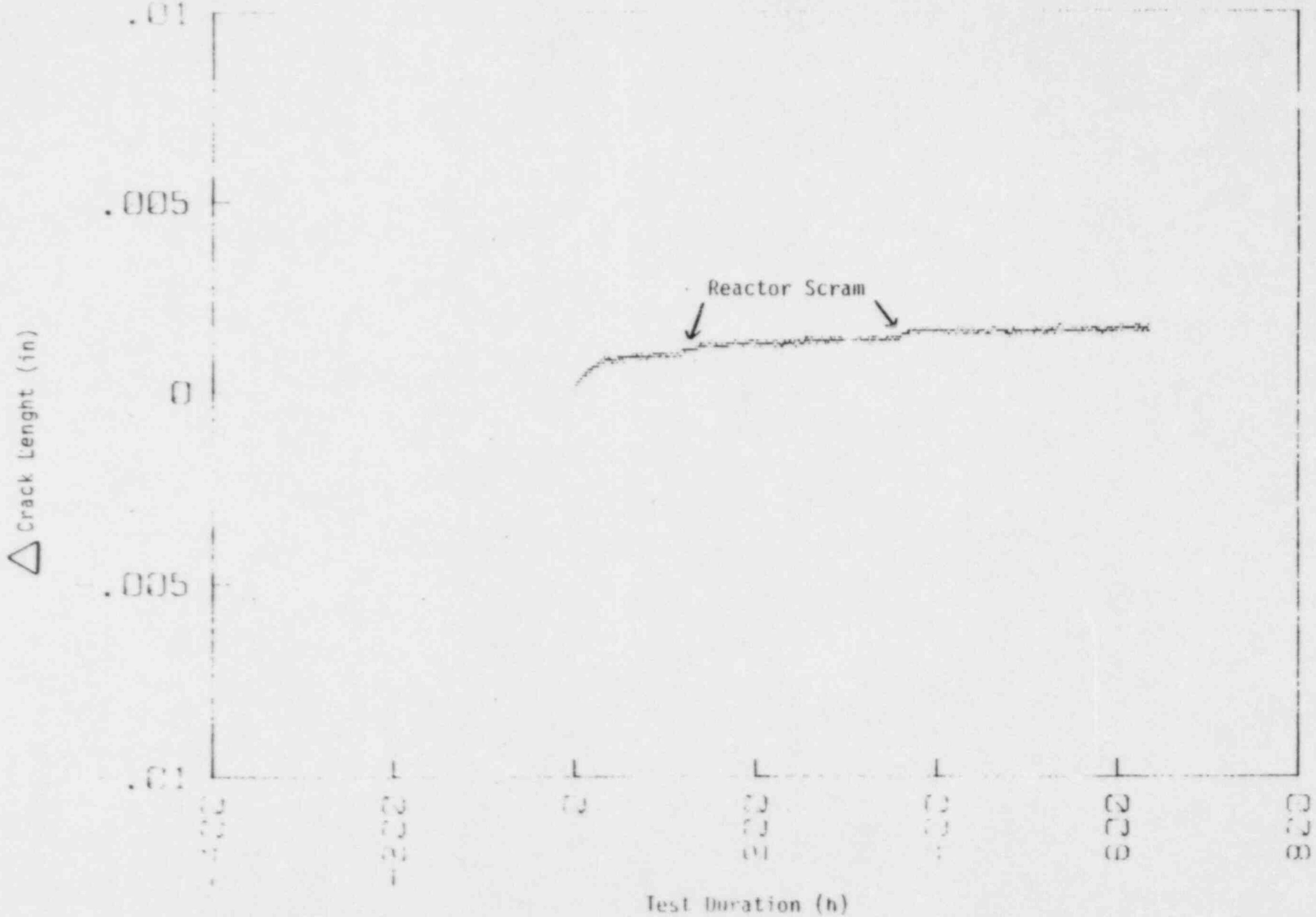
Mid-Cycle ISI Results from Dresden-2

ISI RESULTS

	Date	
Weld	April 29, 1983	November 12, 1983
28" Safe End PS2-201-1	1" long, 16% deep[1]	1" long, 13% deep
12" Riser (Two Cracks) PD5-D20	0.25" long, 17% deep 0.25" long, 19% deep	0.25" long, 15% deep 0.25" long, 17% deep
12" Riser (Two Cracks) PD5-D5	0.50" long, 19% deep 0.25" long, 14% deep	0.50" long, 18% deep 0.25" long, 16% deep

[1] Percentage Through Wall

Figure 1 Dresden-2 HWC Crack Growth Test on Furnace Sensitized Type 304 Stainless Steel, K = 27.5 MPa/m



TECHNICAL BASIS FOR HYDROGEN WATER CHEMISTRY SPECIFICATION

1.0 INTRODUCTION

The recirculating coolant in BWRs is high-purity, (no additive) neutral pH water containing radiolytically produced dissolved oxygen (100-300 ppb). This level of dissolved oxygen is sufficient to provide the electrochemical driving force needed to promote IGSCC of sensitized austenitic stainless steel piping and similar structural components if the other two prerequisities for IGSCC [a sensitized microstructure (chromium depletion at the grain boundaries) and a tensile stress above the yield stress] also are present. A variety of IGSCC remedies has been developed and qualified which address the sensitization and tensile stress aspects of stress corrosion cracking, including Nuclear Grade Type 316 and 304 stainless steels, solution heat treatment (SHT), corrosion-resistant cladding (CRC), heat sink welding (HSW) and induction heating stress improvement (IHSI). It should also be possible to suppress IGSCC by reducing the electrochemical driving force for IGSCC, i.e., by modifying the BWR coolant environment.

The demonstration of an IGSCC remedy based on modifying the chemistry of the BWR coolant is the objective of this materials program. The basic concept is to reduce the aggressiveness of the BWR environment by adding hydrogen gas to the feedwater to reduce the dissolved oxygen concentration in the reactor water, and reduce the coolant conductivity to a low value by improved operational practices. This approach appears to have the potential for "blanket" protection of all types of BWR structural materials during power operation of the plant and may arrest the growth of incipient cracks.

To accomplish the project objective of evaluating and quantifying the beneficial effects of oxygen suppression through hydrogen addition, numerous laboratory and Dresden-2 in-reactor testing techniques have been used to study a broad range of BWR structural materials and corrosion phenomena. The results of these laboratory materials programs and Dresden-2 operational results are the subject of this chapter.

2.0 FULL-SIZE WELDED STAINLESS STEEL PIPE TESTS

2.1 INTRODUCTION

Pipe testing has been performed to quantify the effect of hydrogen water chemistry (HWC) on the IGSCC performance of Type 304 stainless steel piping. The general approach is similar to that used for the General Electric/EPRI Program, "Alternate Alloys for BWR Pipe Applications,"[1] EPRI Project RP-968. However, instead of selecting and qualifying a particular alternative piping alloy, the thrust of the present program was to qualify an alternative environment using hydrogen addition to reduce the dissolved oxygen concentration.

To reliably demonstrate the improved IGSCC performance of Type 304 stainless steel in HWC in a reasonable period of time, a reliable, accelerated test representative of actual field piping conditions was required. The full-size welded pipe test which was developed for EPRI RP-968 fits this requirement. A statistical method was used for developing factors of improvement (FOI) by comparing times-to-failure for an alternate alloy with similar data for the reference alloy, Type 304 stainless steel. Similarly, the method was used to establish a FOI for HWC vis-a-vis the normal 200 ppb O_2/288°C (550°F) BWR steady-state environment by comparing times-to-failure for the reference alloy in the two environments.

2.2 RESULTS AND DISCUSSION

The pipes tests were conducted in simulated BWR high temperature water environments in the Pipe Test Laboratory (PTL) as described in detail elsewhere.[2] This facility was modified to provide control and monitoring capability for hydrogen addition and the lower oxygen and conductivity levels required for HWC.

Initially, the HWC environment selected was 50-70 ppb 0 with a conductivity of 0.6 ± 0.3 uS/cm. This environment was established at a time when it was not certain if lower 0_2 levels could economically be established in a plant and was expected to provide conservative data. Four HWC crack growth specimens, six HWC crack initiation specimens and four reference specimens exposed to 200 ppb 0_2 environments were initially included in the program. Of the four crack growth specimens, two were sectioned metallographically after precracking in 200 ppb 0_2 water to determine pre-crack depth and two were continued on test in the 50-70 ppb 0_2 HWC environment.

As described in additional detail later in this section, premature cracking occurred in the initial 50-70 ppb 0_2 HWC environment and it was determined that dissolved oxygen and conductivity must be lowered to 20 ppb and <0.2 uS/cm, respectively, to demonstrate improvement. Exposure of all cracked specimens was then continued in the new HWC specification environment to determine if crack arrest would occur. Additionally, two new crack growth specimens and three new crack initiation specimens were added to the program for testing in the new HWC environment.

The specifications for the three high temperature water environments used were as follows:

Initial HWC Environment:	
Temperature	282°C ± 5°C (540°F ± 10°F)
Dissolved Oxygen	50-70 ppb
Dissolved Hydrogen	125 ± 25 ppb
Conductivity at 25°C (77°F)	0.6 ± 0.3 uS/cm

Later HWC Environment:	
Temperature	282°C ± 5°C (540°F ± 10°F)
Dissolved Oxygen	15 ± 10 ppb
Dissolved Hydrogen	125 ± 25 ppb
Conductivity at 25°C (77°F)	<0.2 uS/cm

Reference Environment:

Temperature	282°C ± 5°C (540°F ± 10°F)
Dissolved Oxygen	0.2 ± 0.1 ppm
Conductivity at 25°C (77°F)	0.6 ± 0.3 uS/cm

The total test matrix is shown in Table 1. Four heats of Type 304 stainless steel were included in the program. One heat of Type 316 Nuclear Grade stainless steel was included in the crack initiation tests.

The 10-cm (4-in.) Schedule 80 pipe specimens were assembled using eleven 10-cm (4-in.)-long test pieces from one heat, two transition pieces, and top and bottom end caps joined by circumferential welds as illustrated in Figure 1.

The pipe specimens were cyclically loaded at one cycle per day in a pipe test stand, Figure 2. The loading waveform is shown in Figure 3. A long hold time was used to prevent fatigue failure during long exposure to develop FOI. To accelerate cracking, axial test loads were applied to attain a maximum nominal pipe section stress equal to 233.2 MPa (33.8 ksi) $2S_M$ (S_M = ASME Code allowable), as determined at the smallest cross section of the specimen, the weld counterbore.

The results were evaluated by ultrasonic testing (UT) and metallography. Specimens were given an initial baseline UT before going on test. The pipe tests were conducted until through-wall cracks occurred or until the test objectives were achieved and removed for destructive metallographic evaluation. The longer exposure specimens were periodically removed from test for UT inspection to estimate crack growth.

Crack growth pipe specimen AWC-1 failed by IGSCC at HAZ location designated J-1 after 30 cycles, 844 hours exposure to the 50-70 ppb 0_2/0.6 uS/cm conductivity HWC environment described above. This specimen had a precrack initiated in the 200 ppb oxygen environment estimated by UT evaluation to be

0.38 mm (15 mils) deep. During the 50 to 70 ppb O_2/0.6 uS/cm conductivity HWC exposure, the inter granular portion of the crack grew to a maximum depth of 4.8 mm (190 mils) and extended to 360° around the pipe, after which the pipe failed in ductile tension.

Because failure of specimen AWC-1 occurred earlier than expected for HWC exposure, testing of all pipe specimens in this environment was interrupted and UT evaluations were conducted. Table 2 lists the accumulated exposures of the specimens and estimated maximum crack depths from UT inspections.

It can be seen that all specimens tested in the 50 to 70 ppb O_2 high conductivity HWC environment exhibited early cracking except specimen AWC-14, which was fabricated from Type 316 Nuclear Grade (NG) stainless steel pipe. This specimen showed no crack indications during UT examination at maximum sensitivity. Subsequent metallographic examination on specimen AWC-14 verified the UT results.

The remaining unfailed, but cracked specimens from this environment were transferred to the lower oxygen/conductivity environment described above to determine if crack arrest would occur in this environment.

The results of exposure of the precracked specimens to typically 20 ppb O_2/0.2 uS/cm conductivity environment are also listed in Table 2. None of these specimens failed during exposure times significantly longer than the failure times for the four reference 200 ppb oxygenated water specimens listed in Table 2. All of the precracked specimens except AWC-11 and AWC-10 showed some crack extension in the lower oxygen environment. Specimens AWC-9 and AWC-12 had one weld removed from each four metallographic sectioning to characterize the cracking.

The metallographic sections of specimens AWC-9 and AWC-12 showed intergranular cracks with a transition to transgranular during the latter stage of cracking. SEM examination also showed intergranular thumbnail cracks with a transition through mixed mode to total transgranular cleavage fracture at the root of the cracks and, in most instances, showed striations which are indicative of fatigue associated with the cleavage fracture. Since fatigue is not a factor in BWRs, no crack extension would be anticipated.

Two additional crack growth specimens (AWC-15 and AWC-16) were precracked in 0.2 ppm O_2 water to depths of approximately 1.27 and 1.02 mm (50 and 40 mils), respectively. Specimen AWC-15 was exposed to the low oxygen/conductivity H_2WC environment for 5310 hours (including 343 hours in 200 ppb O_2) and specimen AWC-16 was exposed to the 0.2 ppm O_2 water control environment at constant load to evaluate the fatigue component of crack propagation. Specimen AWC-16 failed in 1285 hours, while the precracked specimen AWC-15 did not fail during the total 5653 hours of exposure.

Due to premature failure of the original crack initiation specimens in the 50-70 ppb O_2 water, three new crack initiation specimens (one from each of three heats, specimens AWC-17, -18, and -19) were tested in the low oxygen/conductivity environment. Specimen AWC-17 was removed from test after 1693 hours for interim UT examination and removal of one weld for dye penetrant testing and sectioning. No evidence of crack initiation could be seen at this time. It was repaired and returned to test. Specimens AWC-17, -18, and -19 have obtained 5122, 7580, and 7585 hours of exposure respectively, with no UT indications of cracking. IGSCC would be expected in the norminal environment after ~300 hours (FOI of at least 25). Through wall failures of these pipes in the reference environment would be expected in approximately 1500 hours.

2.3 CONCLUSIONS

The welded pipe test program has revealed the following conclusions to date:

1. For Type 304 stainless steel welded pipe with deep IGSCC, subsequent exposure to a hydrogen water chemistry environment will arrest intergranular propagation even at stress levels of twice the ASME code allowable (i.e., $2S_m$).

2. The factor-of-improvement based on crack initiation data for the HWC environment compared with the nominal environment is at least 25. Also no failures have been observed in HWC initiation pipe tests with exposures of ~7600 hours, whereas pipes tested in the nominal environment fail through wall in approximately one fifth that exposure period.

3. No severely pre-cracked Type 304 stainless steel pipes have failed in the HWC environment.

4. Welded Type 316 Nuclear Grade pipe showed the expected good IGSCC performance in hydrogen water chemistry, with no cracking initiated in 4047 hours at a stress of $2S_m$.

3.0 CRACK PROPAGATION STUDIES

3.1 INTRODUCTION

The series of tests performed under the general heading of crack propagation studies had two major objectives: (1) determine the effects of a reduction in the dissolved oxygen level in the coolant on the crack propagation rates for key BWR structural materials, and (2) determine the crack arrest and retardation behavior in this reduced oxygen environment. The types of testing techniques utilized to provide this information included low cycle fatigue tests, constant load stress corrosion crack growth tests and fatigue crack growth tests.

3.2 RESULTS AND DISCUSSION

3.2.1 Low Cycle Fatigue Tests on Carbon Steel

A series of fatigue crack initiation tests was performed to determine the effect of dissolved oxygen on the fatigue lifetime of carbon steel piping in high purity water. Tests were conducted on notched and unnotched specimens of SA 106-B carbon steel at low (11.1 cph) and high (277 cph) frequencies.

The specimens were cyclically loaded with a R* ratio of 0.08.

$*R = \frac{\text{minimum load}}{\text{maximum load}}$

The test revealed that HWC should not adversely affect the notched or unnotched fatigue crack initiation behavior of carbon steels. Indeed a HWC specification of 20 ppb O_2 and 0.2 uS/cm conductivity clearly inhibits crack initiation and lifetimes approach those obtained in air tests. The service lifetime of carbon steel piping in BWRs probably can be extended by controlling the dissolved oxygen and conductivity levels to low values.

3.2.2 Stress Corrosion Crack Growth Tests

One standard 1T-WOL specimen (Figure 4) was fabricated from each of four typical BWR structual materials: (1) furnace sensitized [621°C (1150°F)/12 h] Type 304 stainless steel; (2) furnace sensitized [621°C (1150°F)/2h] Type 316 Nuclear Grade stainless steel; (3) SA508 Class 2 low alloy steel; (4) SA333 Grade 6 carbon steel. Each specimen was fatigue precracked in room temperature air to ensure that an active fatigue crack was present prior to environmental testing.

The SCC test was performed in six loading phases (three slow cyclic loading phases and three constant load phases) as shown in Figures 5a, b, c. The slow cyclic loading (SCL) phase prior to each of the three constant load (CL) phases ensured that each specimen had an active crack growing in the environment prior to switching to constant load. The loading during each of the constant load phases was selected so that the stress intensity (K) for each specimen corresponded to the K levels used in previous 288°C (550°F)/200 ppb oxygenated water baseline tests.[3] Therefore, a direct comparison of crack growth rates in the 200 ppb oxygenated water baseline environment and HWC could be made. The results of these tests are summarized in Tables 3 and 4 for the HWC and nominal environment, respectively.

The results of the SCC growth tests revealed that the HWC environment was detectably less aggressive than the 200 ppb O_2 environment for three of the four matrials tested; the Type 316 Nuclear Grade stainless steel showed no detectable growth in either environment.

3.2.3 Fatigue Crack Growth Tests

A total of ten compact tension (CT) fracture mechanics specimens and two 1T-WOL fracture mechanics specimen were tested at two cyclic frequencies. Each specimen was fatigue precracked a minimum of 1.9 mm (0.075 in.) in room temperature air to ensure that an active fatigue crack was present prior to testing in the HWC environment. The materials tested were annealed, furnace sensitized, welded and low temperature sensitized [482°C (900°F)/24 h] Type 304 stainless steel, furnace sensitized Type 316 Nuclear Grade stainless steel, SA508 Class II low alloy steel and SA333 Grade 6 carbon steel (only 1T-WOL specimens).

Six specimens were loaded at a time in a series chain using the skewed sawtooth waveform shown in Figure 6. The cyclical frequency was 0.74 cph (81-minute period) and 7.5 cph (8-minute period) with R = 0.6. Initial stress intensity values were selected to obtain a direct comparison of crack growth rates in HWC with growth rates generated previously for the same materials in a 200 ppb oxygenated water environment under identical loading conditions.

The six 0.74 cph specimens were subjected to 1349 loading cycles in HWC while the remaining 7.5 cph specimens were characterized by 15,000 cycles. Compliance-based crack length data for the twelve specimens, as well as eight specimens tested in the nominal environment, were analyzed for average crack growth rate as shown in Table 5. These average cyclic crack growth rates are plotted as a function of stress intensity range (K) in Figures 7 through 10 for austenitic stainless steels and ferritic materials at the two cyclic frequencies.

Figure 7 shows that the 0.74 cyclic crack growth rates for the two sensitized Type 304 stainless steel specimens tested in 200 ppb O_2 reference environment were three times greater than the cyclic crack growth rate of sensitized Type 304 stainless steel tested in HWC. The solution annealed and weld HAZ Type 304 stainless steel specimens which had a low degree of sensitization had HWC cyclic crack growth rates similar to the specimen which was highly sensitized. Therefore, the degree of sensitization of Type 304 stainless steel seems to have little effect on cyclic crack growth rate in HWC under the loading conditions tested. The cyclic crack growth rate for Type 316 Nuclear Grade stainless steel in HWC was only slightly less than the Type 304 stainless steel data.

A more dramatic difference in cyclic crack growth rate in HWC versus the 200 ppb O_2 reference environment was seen in the carbon steel and low alloy steel specimens, Figure 9. The 0.74 cyclic crack growth rate in HWC was 20 times less for carbon steel and 7 times less for low alloy steel than in the 200 ppb O_2 reference environment. Similar differences in cyclic crack growth in HWC versus the 200 ppb 0_2reference enviroment was seen at higher 7.5 cph where the factor of improvement for Type 304 stainless steel was similar to that obtained at the lower frequency, but significantly higher (450 and 1000X) for the ferritic materials, Figures 9 and 10.

3.2.4 Slow Rising Load (SRL) Fracture Mechanics Tests

The H_2WC crack growth test was designed to duplicate the test conditions of a previous SRL test conducted in the nominal 0.2 ppm oxygenated water environment.' In this way, a direct comparison of results could be made between the two different environments. In this task, the 1T-CT test was performed in a water environment containing 230 ppb H_2 and 50 ppb oxygen at 288°C (550°F).

Both tests were performed using standard linear elastic fracture mechanics type crack growth specimens made from SA508 Class II low alloy steel. However, the specimens were clad with stainless steel so that any electrochemical potential differences between the cladding and base metal materials would be established during testing.

In situ compliance measurements of the 1T-CT specimen tested by the slow rising load method indicated no apparent crack growth during the entire 800 hours of loading in the hydrogen modified high temperature aqueous environment. In contrast, a similar specimen tested in water with 0.2 ppm O_2 showed a crack extension of ~0.36 mm (0.014 in.) in a test period of 880 hours. Except for the dissolved oxygen and hydrogen levels, the conditions for both tests were the same. The crack growth data are shown in Figure 11.

After test termination, the 1T-CTs were split apart mechanically to determine whether any pre-crack extension had occurred. The sample tested in the simulated BWR environment indicated crack growth in the base metal to approximately the extent predicted by the compliance measurements, while the sample tested in the hydrogen modified environment showed no crack propagation.

3.2.5 Bolt Loaded 1/2 T-WOL Fracture Mechanics Tests

Triplicate bolt-loaded 1/2 T-WOL [1.77 cm (0.5 in.)-thick wedge opening loading WOL] specimens were fabricated from carbon steel and two low alloy steels. The low alloy steel specimens contained Type 309 stainless steel weld metal in the precracked region and had Type 304 stainless steel plates tack welded to their surfaces to simulate a stainless steel clad component.

Duplicate bolt-loaded WOLs of the carbon and low alloy steels (6 specimens) were tested in a refreshed stainless steel autoclave system that contained water at 288°C (550°F) with 140 to 258 ppb H_2 and 7 to 11 ppb dissolved O_2. The conductivity was controlled to <0.2 uS/cm. The third set of three WOLs was tested during the hydrogen injection program at Dresden-2 from 5/19/82 to 6/29/82.[5] The stress intensity was 58.1 MPa /in(52.9 ksi /in).

Tests from duplicate bolt-loaded specimens of three materials (SA106-B, Clad SA533-B and Clad SA508-2) showed no crack growth after 5521 hours and the absence of crack growth was verified metallographically. Results from the set of three specimens which were exposed during the H_2 injection program at Dresden-2 also showed no crack propagation after 936 hours of exposure, in spite of the fact that there were occasional high dissolved O_2 concentrations during the testing period.

3.2.6 Potential Drop Fracture Mechanics Tests

This investigation was designed to determine the response of SA533-B low alloy steel in HWC (50 ppb O_2 and 125 H_2, <0.2 uS/cm) under constant load, using the potential drop technique to monitor crack growth. Compact tension specimens were machined with a 0.05 mm (2 mil) radius notch and were instrumented for both in-situ crack opening displacement (for use with the compliance technique) and DC potential drop monitoring. A reversed DC potential drop technique was used which involved reversing the current flow through the sample every 0.5 to 1 sec both to minimize electrochemical effects and to reduce measurement errors associated with thermocouple effects, etc. The test was initiated under constant load conditions at 55 MPa /m (50 ksi /in.). No crack growth was observed either with the DC potential drop growth monitoring technique or with the linear variable differential transformer (LVDT) crack opening displacement gage. After approximately 50 hours, the load was increased to 47.8 kN (10,740 lb), resulting in a stress intensity of 60.4 MPa /m (55 ksi /in.). After one week of exposure, neither crack opening displacement nor DC potential measurements indicated any crack growth, so the load was raised again to 52.5 kN (11,800 lb) or 66 MPa /m (60 ksi /in.). After more than 1500 hours of exposure at this level, there was no in-situ indication of crack growth.

The sample was removed from the autoclave system, examined and photographed, and then pulled apart after sawing a two centimeter notch from the back face of the specimen and cooling the specimen in liquid nitrogen. Examination of the specimen after separation showed that no cracking of the metal at the base of the notch occured.

This test shows that the low alloy steel SA533-B is extremely resistant to cracking in hydrogen water chemistry at 288°C (550°F) under constant load conditions. This result compares favorably with those obtained on low alloy steel at 288°C (550°F) in water containing 0.2 ppm or 8 ppm oxygen. At 8 ppm oxygen, crack growth was observed under cyclic load and constant load at stress intensiy values above approximately 33 MPa /m (30 ksi /in.). In water containing 0.2 ppm oxygen, no growth was observed under constant load at stress intensity values up to 63.7 MPa /m (58 ksi /in.), although under cyclic loading crack growth occurred at stress intensity values as low as 41.8 MPa /m (38 ksi /in.).

3.3 CONCLUSIONS

The results of the various laboratory test series designed to evaluate the effects of HWC on crack propagation rates in typical BWR structural materials can be summarized as follows:

1. Reducing the oxygen content does not adversely affect the notched or unnotched fatigue crack initiation behavior of carbon steel and the fatigue performance may improve at the low oxygen levels involved in HWC.

2. Under constant loading conditions, no measurable crack growth was detected in the HWC environment for furnace-sensitized Type-304 stainless steel, furnace-sensitized Type 316 Nuclear Grade stainless steel, SA508 Cl.II low alloy steel and SA333 Gr. 6 carbon steel for stress intensities up to 31.2 MPa /m (28.4 ksi /in.), 30.1 MPa /m (27.4 ksi /in.), 50.9 MPa /m (46.3 ksi /in.) and 44.8 MPa /m (40.3 ksi /in.), respectively. In the nominal enviornment, measurable crack growth is observed at significantly lower stress intensities for furnace-sensitized Type 304 stainless steel [16.3 MPa /m (15.7 ksi /in.)] and is observed on SA206-B carbon steel at 44.0 MPa /m (40.0 ksi /in.). No measurable crack growth occurs in the low alloy steel or the Type 316 Nuclear Grade stainless steel in the nominal environment.

3. The 0.74 cph cyclic crack propagation rates for furnace-sensitized Type 304 stainless steel, SA508-Cl.II low alloy steel and SA333 Gr. 6 carbon steel were respectively 3, 7 and 20 times slower in the HWC environment than in the nominal BWR environment. At 7.5 cph, the cyclic crack propagation rate for furnace-sensitized Type 304 stainless steel was also ~3, while for the ferritic low alloy and carbon steel the crack propagation rates were ~450 and 1000 times slower, respectively.

4. In the HWC environment no crack growth occurs in pre-cracked low alloy steel specimens clad with Type 309 stainless steel loaded to a high stress intensity, 58.1 MPa /m, (52.9 ksi /in.).

5. The presence of hydrogen gas dissolved in the coolant does not increase the crack growth rates of SA106-8 carbon steel, clad SA533-B, and clad SA508-2 low alloy steel.

6. DC potential drop and LVDT crack opening displacement techniques used to monitor crack length in compact tension samples of low alloy steel SA533-B under constant load conditions at 288°C (550°F) in pure water containing 50 ppb oxygen and 130 ppb hydrogen, revealed no crack growth after 160 hours at 60.4 MPa /m (55 ksi /in.) or after >1500 hours at 66 MPa /m (60 ksi /in.).

Overall, the results indicate that materials which are susceptible to environmentally-assisted crack growth in the nominal BWR environment perform better under HWC conditions, i.e., the hydrogen water chemistry environment is less aggressive than the nominal environment with respect to environmentally-assisted crack growth in BWR structural materials.

4.0 CORROSION POTENTIAL MEASUREMENTS AND SLOW STRAIN RATE TESTS (CERT AND SET)

4.1 INTRODUCTION

The objective of this part of the program was to determine whether stress corrosion or other forms of localized corrosive attack can occur in HWC. The task included three subtasks: (1) measurement of the corrosion potentials of Type 304 stainless steel. Alloy 600, carbon steel, Zircaloy-2, and low chromium (simulated sensitized grain boundary) Type 304 stainless steel in six water environments covering the expected range of HWC dissolved oxygen and hydrogen contents; (2) Constant Extension Rate Technique (CERT) testing of Type 304 stainless steel, Alloy 600 and low alloy and carbon steels, in three O_2-H_2 water environments selected from subtask (1), plus additional CERT tests on low alloy and carbon steel to support the Dresden-2 tests and (3) limited Straining Electrode Technique (SET) testing of Type 304 stainless steel, Alloy 600 and Alloy X-750 at various test potentials simulating the nominal and HWC environments.

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4.2 RESULTS AND DISCUSSIONS

4.2.1 Corrosion Potential Measurements

The decrease in dissolved oxygen content in the BWR coolant as a result of hydrogen addition to the feedwater should significantly reduce the corrosion potential, which is a measure of the thermodynamic driving force for corrosion reactions. Figure 12, from Indig and McIlree[8], indicates that there is a rapid drop in the corrosion potential of Type 304 stainless steel when the dissolved oxygen content falls below approximately 40 ppb.

The corrosion potentials of Type 304 stainless steel, Alloy 600, carbon steel (SA333, Gr. 6), Fe-10Ni-8.1Cr, Zircaloy-2 and platinum were measured against a high temperature Ag/AgCl reference electrode in high purity water and in a 0.01N Na_2SO_4 solution. The high purity water and sodium sulfate solutions contained specific concentrations of dissolved oxygen and hydrogen and were heated to 274°C (525°F). In the Na_2SO_4 solutions, the potential of pressure vessel steel (SA533 Gr. B) was also determined. Table 6 presents a list of the bottled gases used in this study and calculated dissolved gas concentrations in the test environment.

In high purity water, the electrochemical potentials for stainless steel tended to be below the potentials previously obtained when the dissolved oxygen concentration was >100 ppb. At very low dissolved oxygen concentrations, the opposite effect occurred; the potentials were above previous values. The other iron and nickel base alloys behaved similarly. The net effect was to limit the response of electrochemical potential with changing dissolved oxygen concentration. The corrosion potentials in 0.01 N Na_2SO_4 were lower than in high purity water. In part, this decrease in potential is related to an increase in pH because the Na_2SO_4 forms a basic solution in high temperature water. It appeared that hydrogen had only an indirect effect on the electrochemical potential of the corrosion electrodes as measured in these laboratory tests. In the reactor, the major effect of hydrogen will be in recombination with oxygen, and, as the oxygen decreases, a decrease in the chemical driving force for IGSCC will be observed.

4.2.2 Constant Extension Rate Tests

The constant extension rate test (CERT) facility used for studying stress corrosion cracking behavior of alloys in simulated BWR environments was described by Clarke, Cowan, and Danko.[7] To minimize oxygen gettering due to chemical reaction with heated surfaces, the regenerative heat exchanger was fabricated from titanium tubing and the pressure vessel and load frame internals were made from Ti-6Al-4V alloy.

All CERTs (apart from the Dresden-2 support tests) were conducted at 274°C (525°F) in controlled aqueous environments (both water purity and various dissolved gas concentrations) at a strain rate of $2X10^{-5}$ min^{-1}. CERTs were conducted on Type 304 stainless, Alloy 600, pressure vessel low alloy steel (SA533) and carbon steel SA333, Gr. 6.

Table 7 presents a summary of the experimental conditions and the CERT results for the materials tested. The CERT results tabulated are the mechanical properties, failure times, and failure morphologies. Lower values of the mechanical properties and shorter CERT testing times are indications of stress corrosion cracking. Verification of stress corrosion cracking is obtained by post-test examination.

The most important result of these tests was that none of the alloys exhibited any sign of stress corrosion cracking in the hydrogen water chemistry environment. Except for Alloy 600, all of the alloys exhibited some degree of stress cracking in a simulated normal BWR environment.

The laboratory CERT tests performed in support of the Dresden-2 HWC demonstration used SA508 Class II, SA533 Grade B Class I low alloy steel and SA106 Grade B carbon steel tested in the creviced and uncreviced condition. The crevice was produced by wrapping and spot welding thin stainless steel shim stock around the test section. The test conditions and results are presented in Table 8. Comparison of these data with previous low alloy steel CERT data in 200 ppb O_2 water, 8.0 ppm O_2 water and air shows the benefit of the HWC (50 ppb O_2, 230 ppb H_2, <1 uS/cm).[5] In contrast to the roughly 20% transgranular stress corrosion cracking (TGSCC) in 0.2 ppm O_2, these HWC CERT test results reveal the 100% ductile behavior and appear to be essentially the same as 288°C (550°F) air test results.

The CERTs clearly indicated that in high purity water, intergranular stress corrosion cracking of weld-sensitized Type 304 stainless steel and TGSCC of pressure vessel and carbon steel can be prevented by hydrogen water chemistry.

The indications from CERTs carried out in the present and previous programs are that the low alloy and carbon steel are more resistant to stress corrosion cracking in higher dissolved oxygen concentrations than stainless steel.

Alloy 600 in the welded + LTS condition did not show any indications of IGSCC in any of the CERTs. This was not surprising, since the only instance of IGSCC of this alloy in the field was related to the presence of crevice and high concentrations of an impurity (resins).

4.2.3 Straining Electrode Tests

The straining electrode test (SET) is a CERT conducted under potential control rather than chemical control. Because potential control requires the passage of current through the solution in contact with the specimen, a conductive electrolyte is used to minimize IR drops. A circulating deaerated 0.01N solution of Na_2SO_4 maintained at 274°C (525°F) was the electrolyte. The control potentials simulated either normal BWR or HWC environments. All specimens were pulled to failure at a strain rate of $2X10^{-5}$ min^{-1} in an austenitic stainless steel pressure vessel. Since deaerated test solutions were used, titanium alloys in the high temperature SET system were not necessary. Figure 13 is a sketch of the SET facility and Table 9 presents the test matrix.

The results of the SETs are presented in Table 10. The critical findings in these tests were that no SCC occurred at potentials that simulated the hydrogen water chemistry environment for Type 304 stainless steel, Alloy 600 or Alloy X-750. IGSCC did occur in the simulated nominal environment for Type 304 stainless steel and Alloy 600. No cracking of Alloy X-750 occurred in the SETs at -0.100 and $-0.700V_{SHE}$. The low potential $-0.700V_{SHE}$ was used to determine whether hydrogen embrittlement could occur in this high strength alloy at potentials somewhat below those expected under hydrogen water chemistry.

4.3 CONCLUSIONS

The results of the electrochemical measurements, CERTs and SETs indicate the following conclusions relative to the effects of HWC on BWR structural materials:

1. The major finding in the stress corrosion testing under chemical and electrochemical control in high purity water was that under simulated hydrogen water chemistry conditions, IGSCC of weld-sensitized and welded-plus-LTS Type 304 stainless steel and Alloy 600 and TGSCC of low alloy steel were eliminated. In simulated normal BWR water, SCC of these materials occurred. SCC under electrochemical control with a supporting electrolyte (0.01N Na_2SO_4) was far more severe than under chemical (oxygen) control in high purity water.

2. HWC appears to suppress the transgranular stress corrosion cracking of creviced or uncreviced specimens of SA533-B and SA508 Class II low alloy steels and SA106-B carbon steel, which is observed in the nominal environment.

3. No SCC was found for welded and low temperature sensitized specimens of Type 304 stainless steel and Alloy 600 at electrochemical potentials of $-500\ mV_{SHE}$ (a simulated HWC environment), while cracking was observed for both materials in

the simulated normal BWR environment at -100 mV_{SHE}.

4. No hydrogen stress cracking was found for Alloy X-750 at potentials simulating deaerated water with a high dissolved hydrogen content (-700 mV_{SHE}) and no SCC was observed for this alloy in the nominal BWR environment (-100 mV_{SHE}).

5.0 DRESDEN-2 HWC TEST RESULTS

5.1 INTRODUCTION

Materials tests have been conducted at Dresden-2 under HWC conditions to confirm the results of the laboratory HWC investigations. These tests indicate that laboratory data appear to be directly applicable for predicting materials behavior in an operating BWR.

The first set of hydrogen injection verification studies were run at the Dresden-2 nuclear power plant of the Commonwealth Edison Co. from May 19 to July 7, 1982. Hydrogen was added to the reactor feedwater via injection taps in the condensate booster pump casings. Initially hydrogen was added for five consecutive steady-state periods during which feedwater hydrogen concentrations in parts per billion were: <5 (two days), 200 (two days), 400 (two days), 1000 (four hours) and 1800 (four hours). Reactor power during this sequence was held at about 83% of full power (2527 MWTh).

The remainder of the initial demonstration testing with hydrogen was done from June 3 to June 29 to support electrochemical potential (ECP) measurements and CERT tests in the reactor autoclaves. Except for power decreases for maintenance or weekend surveillance testing, reactor power was close to 100% during this time. The hydrogen addition rate was adjusted to produce the required oxygen concentrations in the test autoclaves (reactor recirculation system water) and ranged from 0.6 to 1.3 ppm in the reactor feedwater. After the cessation of hydrogen addition, there were 10 additional days of CERT testing under normal reactor conditions to provide baseline comparison data.

In April 1983, Dresden-2 initiated full time operation on hydrogen water chemistry. From October 1983 through April 1984, a second series of ECP measurements and CERT tests were performed in the same reactor autoclaves.

5.2 DRESDEN-2 MATERIALS RESULTS

5.2.1 Corrosion Potential Measurements

Electrochemical potentials (ECP) of Type 304 stainless steel, Alloy 600, SA533-B low alloy steel, and platinum were measured against an AgCl reference electrode in an autoclave containing flowing reactor water. In general, the ECPs decreased directly with oxygen concentrations in a manner similar to that obtained in the laboratory, Figure 14. With time, however, at any constant oxygen concentration and conductivity, the corrosion potential of film-forming materials drifted upward. The platinum potential was unique and more sensitive to hydrogen than oxygen concentration. Based on these potential measurements, and the stress corrosion cracking results (discussed below), it appears that intergranular stress corrosion cracking (IGSCC) of furnace-sensitized Type 304 stainless steel in boiling water reactors can be prevented at corrosion potentials less than $-0.325V_{SHE}$, in agreement with the laboratory test data presented earlier.

During the second ECP measurement campaign at Dresden-2 (October 1983 - April 1984), the ECP of stainless steel was measured for 3330 hours (~139 days), Table 11. The potentials obtained during this extensive coverage were similar to those measured during the first demonstration campaign. The normal Dresden-2 environment was characterized by an ECP range for Type 304 stainless steel of -100 to -200 mV_{SHE}, while the hydrogenated Dresden-2 environment reduce the Type 304 stainless steel potential to -370 to -460 mV_{SHE}. Table 11 also presents the average ECP values obtained for Type 304 stainless steel and platinum during this test period while Table 12 presents some typical values for working electrodes for a one month measurement period.

The "memory" effect noted in Table 11 is very important. It appears that during times when HWC is terminated, a "memory" effect occurs in that the potential does not suddenly rise into the range where IGSCC of sensitized Type 304 stainless steel can occur. Instead the potential rises slowly which creates a window of time prior to rising into the cracking potential region. Typically this window is ~10 hours, Figure 15.

The ECP measurements obtained during the second campaign also revealed that at Dresden-2 there is no significant difference between the ECPs of filmed or unfilmed Type 304 stainless steel and Type 316 stainless steel. This differs from some of the data obtained by ASEA-ATOM at Ringhals-1 which suggested that Type 316 stainless steel reaches a significantly lower potential in HWC than Type 304 stainless steel. The behavior at Ringhals-1 may not be real.

5.2.2 CERT Test Results

Two low alloy steel and three furnace-sensitized Type 304 stainless steel specimens were tested in Dresden-2 environments modified by hydrogen injection, and in the normal BWR environment that contained approximately 200 ppb dissolved oxygen during the initial HWC demonstration. In the modified BWR environments, two different H_2 injection rates resulted in dissolved oxygen concentrations of 40 ± 5 and <20 ppb dissolved oxygen. Type 304 stainless steel tensile samples were run in both of the modified environments, while the SA533 Grade B low alloy steel was tested in the aqueous environment that contained <20 ppb O_2.

For Type 304 stainless steel, suppressing the dissolved oxygen to 40 ppb resulted in a decrease in the amount of IGSCC, but elimination of the phenomenon did not occur until the dissolved oxygen concentration was <20 ppb. Stress versus time plots, normalized to a crosshead speed of 25 um/h (0.001 in/h), Figure 16, are shown for the three different reactor environments. The vertical dashed lines indicate the times the load was removed from the tensile specimen when the hydrogen injection system was shut off. The "x"s indicate CERT data obtained in 288°C air. When the curves are converted to stress-strain curves at a crosshead speed of 25 um/hr (0.001 in/h), each 100 hours of the testing results in a 13.3% specimen strain. The curves clearly show the increased ductility and tensile strength (decreased IGSCC) with decreasing dissolved oxygen concentration. The <20 ppb oxygen data is similar to that outlined in high temperature air. The CERT at the lowest dissolved oxygen concentration was terminated before specimen failure.

The low alloy steel samples during the 1982 campaign, clearly showed the benefit of reduced oxygen concentration in stress corrosion response. Both laboratory and in-reactor studies are in agreement as transgranular stress corrosion cracking was eliminated as the oxygen decreased to <20 ppb. Since the pressure vessel steel was tested at 75 um/h (0.003 in/h), each 10 hours of extension should produce about 4% strain. Transgranular cracks were found in the sample tested in the laboratory in water containing 200 ppb dissolved oxygen, but no cracks were found in the samples tested in the laboratory or reactor in the low dissolved oxygen environment. Since low alloy steel is more tolerant of higher oxygen concentrations and lower water purity than sensitized stainless steel, any oxygen-conductivity environment which provides SCC protection for sensitized stainless steel will also provide protection for the low alloy steel.

The 1983-1984 CERT test campaign at Dresden-2 was characterized by a similar set of seven experiments. Four furnace-sensitized Type 304 stainless steel, specimens, one furnace-sensitized Type 304 stainless steel specimen (precracked by IGSCC in a 0.2 ppm oxygen water laboratory autoclave and shipped to the site), one SA106 Grade B carbon steel and one SA508 Class II low alloy steel specimens were tested. The results of these CERT tests plus the results of the first campaign and comparable laboratory tests are summarized in Table 13.

Table 13 clearly indicates an excellent correlation between Dresden-2 and laboratory CERT test results. It also clearly shows that HWC provides mitigation of IGSCC in furnace sensitized Type 304 stainless steel even in instances where hydrogen addition has been interrupted. For example, in one CERT study (line No. 6) 396 hours of test time and 45% strain were accumulated with >10% of the test time in oxygenated water (36 hours with no H_2 and O_2 >200 ppb and 15.5 hours with O_2 at 25-41 ppb) and no IGSCC was identified. However, in CERT No. 5, a 12 hour continuous test period with the hydrogen injection terminated produced minor IGSCC damage. (This test result is also marred by a thermal overload problem which resulted in extremely high thermal stress.) The precracked furnace-sensitized Type 304 stainless steel specimen (No. 8) (67 hours in 200 ppb O_2) which was carefully documented prior to in-reactor testing, failed by ductile tearing after 301 hours in Dresden-2. The mechanical parameter of this specimen is similar to non-precracked specimens. It is also important to note that this test included 10 hours >40 ppb oxygen. Finally, no IGSCC was identified in either SA508-2 and SA533-B low alloy steel and SA106-B carbon steel in HWC at Dresden-2 despite interruptions in hydrogen injections.

5.2.3 DC Potential Drop Crack Growth

Crack growth data versus time and environment on precracked furnace-sensitized Type 304 stainless steel is being obtained at Dresden-2 using the reversing DC potential drop technique as developed by GE Corporate Research and Development. The specimen was precracked in San Jose in the nominal 200 ppb O_2 and then transported to Dresden-2 for testing. The K_I level for the specimen bounds the crack previously identified in Dresden-2 safe-end at 27.5 MPa /m (25 ksi /in). To supplement this program, bolt loaded WOL specimens (one each) of Alloy 600 and unclad SA508 Cl. II low alloy steel have also been inserted into the autoclave.

Figure 17 presents the early DC potential drop crack growth data of the precracked furnace-sensitized Type 304 stainless steel specimen. Although the data is preliminary and is clouded by a reactor scram which occurred approximately 120 hours into the test and some other interruptions in hydrogen injection, no significant crack growth has occurred on the specimen. This preliminary result verifies the result of the Dresden-2 precracked CERT test discussed above and the results of the mid-cycle in-service inspection (ISI) as presented in Table 14.

This mid-cycle ISI was performed as required by the NRC to verify the mitigation of IGSCC growth by HWC. The inspection was performed on November 12, 1983, after approximately 5.5 months of operation with hydrogen injection. The results presented in Table 14 indicate that despite interruptions in hydrogen injection, no crack growth was detected by ultrasonic testing.

5.3 CONCLUSIONS

The Dresden-2 materials tests have revealed the following conclusions relative to the effects of HWC on the structural integrity of actual BWR materials in an operating reactor:

1. The ECPs of all the tested BWR structual materials decrease with decreasing oxygen content. During times when HWC is terminated, a "memory" effect occurs in that the potential of Type 304 stainless steel does not rapidly rise into a range (> $-325\ mV_{SHE}$) where IGSCC can occur. This "safety" window of time appears to be ~10 hours.

2. HWC clearly provides mitigation of IGSCC in furnace sensitized Type 304 stainless steel and TGSCC of carbon steel and low alloy steel at Dresden-2. These results are in exact agreement with laboratory studies.

3. For pre-cracked furnace sensitized Type 304 stainless steel a Dresden-2 CERT test and preliminary DC potential drop studies indicated mitigation of crack propagation in-reactor. These results combined with laboratory pre-cracked pipe tests results and the ISI data at Dresden-2 indicate that pre-existing cracks at Dresden-2 should not propagate during HWC operation.

6.0 ADDITIONAL CORROSION TESTING ON AUSTENITIC, MARTENSITIC AND FERRITIC BWR STRUCTURAL ALLOYS

6.1 INTRODUCTION

The objective of this broad task was to assess the effects of hydrogen water chemistry on the stress corrosion, general corrosion, and crevice and galvanic corrosion of typical austenitic, martensitic, and ferritic BWR structural materials. The effects of notches and defected corrosion films are also being investigated.

PWR work has indicated that very low oxygen levels result in higher general corrosion and metal release rates for carbon and low alloy steels. Also, with hydrogen addition there are some concerns about the possiblity of hydrogen embrittlement. Areas of the BWR reactor system of particular concern are ground (unclad) regions of nozzles, the carbon steel feedwater system and martensitic stainless steel pump and valve components.

This section of the report presents the general corrosion rates and metal-to-system release rates, oxide film analysis and stress corrosion results for the various materials and conditions after eight months exposure and compares the results in HWC and reference water environments containing 200 ppb 0_2 or 8 ppm 0_2.

6.2 RESULTS AND DISCUSSION

6.2.1 General Corrosion - Pre-Filmed Carbon and Low Alloy Steel

To investigate the effect of introducing HWC into an operating BWR with flawed corrosion films on carbon and low alloy steel alloys, rectangular coupons [5.6 x 2.0 x 0.15 cm (2.2 x 0.8 x 0.06 in)] with a hole drilled in one end for hanging were used. The specimens were pre-filmed for 500 hours in 288°C (550°F) water containing 0.2 ppm oxygen. To determine possible effects of a defected pre-film. one-half of the specimens were scratched by a scribe diagonally. corner-to-corner on each side completely through the oxide film. Specimens were exposed in triplicate to the HWC environment (6 to 14 ppb 0_2, 190 to 270 ppb H_2, 0.07 to 0.25 uS/cm conductivity) only. Two heats of both carbon and low alloy steel were used in the "as received" condition. The carbon and low alloy steels showed relatively high initial corrosion rates during the first month (129 to 175 mg/dm^2) followed by steady-state corrosion rates of 8 to 19 mg/dm^2/mo (3744 hours of exposure). In Figure 18, the average corrosion and release rates from zero time are plotted on oxygen dependency curves compiled by Urbanic' from numerous results reported in the literature. The corrosion rates fall within the range of values compiled for 10 ppb oxygen and the metal release rates are a factor of four less than those for 10 ppb oxygen. These rates will decrease with further exposure because of the decreased steady-state corrosion rate once a protective film is formed.

The corrosion and metal release rates were not significantly different for any of the carbon and low alloy steels tested. In addition, scratching of the pre-film showed no effect on corrosion or metal release rates for the materials tested.

The oxygen dependency curves of Urbanic (Figure 18) show that a substantial benefit in corrosion and release rates would result if the oxygen content was increased from 10 to 20 ppb. In BWR feedwater under HWC conditions, achievement of an oxygen content $\geq$ 20 ppb might require oxygen injection.

6.2.2 General, Crevice and Galvanic Corrosion - Austenitic Alloys and Un-Filmed Carbon Steel

Coupons were machined from Type 304 and 316L stainless steel, Alloy 600 and SA333-6 carbon steel pipe wall and used as shown in Figure 19 for the general, crevice, and galvanic corrosion tests. To form the crevice specimens, two coupons were fastened face-to-face with stainless steel screws with a 25 micron (one mil) stainless steel shim placed between the coupons at each end to form a 25 micron (one mil) crevice gap. To determine crevice effects, specimens of like materials were fastened together. Galvanic effects were investigated by fastening specimens of different materials together. The general corrosion specimens were exposed in triplicate and the others in duplicate.

Types 304 and 316L stainless steel specimens showed low corrosion rates and metal-to-system loss in both the simulated normal BWR and HWC environments. The creviced/galvanic condition only resulted in slightly lower initial weight loss for these alloys in both environments.

Alloy 600 showed significantly higher corrosion rates in 200 ppb O_2 water than in the HWC environment, but showed low initial weight loss in both environments. As anticipated, the corrosion rates were higher than for

Types 304 and 316L stainless steel. No effect of crevicing or galvanic coupling was observed for Alloy 600.

Corrosion rates were very low for the unfilmed carbon steel in the reference environment with relatively high initial weight loss, indicating that the corrosion film that forms becomes very protective in the higher oxygen environment. However, corrosion rates were up to about 40 times greater in the HWC environment with correspondingly larger metal-to-system loss. Cervices and galvanic coupling appear to have no significant effect.

6.2.3 Oxide Film Studies

This task involved the analysis of the corrosion film formed on highly polished Type 304 stainless steel, low alloy steel, and carbon steel specimens exposed to nominal (200 ppb O_2) and low O_2 (50 ppb O_2 and 125 ppb H_2) environments. The oxide films were analyzed for thickness and compositional differences after 700 hours of exposure in each environment. Small amounts of cobalt (1 ppb) were added to the test solutions to determine its relative incorporation into the nominal and low O_2 films.

The results of this study indicated that although some differences in the corrosion films on Type 304 stainless steel, SA533-B low alloy steel and SA333 Grade 6 carbon steel can be detected as a result of changes in water chemistry, these differences are not marked after 700-hour exposures. The most significant difference seen was the formation of a thinner film on stainless steel under hydrogen water conditions. The cobalt concentration in the surface films seems to be independent of water chemistry for all these materials, implying no significant change in initial radiation buildup in the low O_2 environment. Somewhat lower concentrations of cobalt are found in the corrosion films that form on alloy and carbon steels than on Type 304 stainless steel under both water chemistry conditions.

6.2.4 Constant Load Tests - Carbon and Low Alloy Steel

Smooth and notched tensile specimens were used in the constant load tests. The lower strength SA106-B and SA333-6 specimens were loaded during test to a net section stress of 190% of the 288°C (550°F) yield stress. The higher strength SA533-B and SA508-II specimens were loaded to a net section stress of 110% of the 288°C (550°F) yield stress to avoid exceeding the ultimate tensile strength. One-half of the specimens were notched, the notch being designed to result in a stress concentration factor K_t, of 2.0.

These constant load specimens were exposed to the same HWC environment as that used in the general corrosion studies. No evidence of hydrogen stress cracking or other adverse effects were observed in either of these two ferritic alloys after 5359 hours of exposure. It appears that these alloys should continue to exhibit the same excellent SCC resistance in HWC as is currently being observed in BWR service.

6.2.5 Constant Load Tests - Austenitic Alloys

The constant load tests on Type 304 and 316L stainless steel and Alloy 600 were performed on the materials in two conditions: (1) furnace-sensitized at 650°C (1202°F) for 24 hours and (2) welded and then low temperature sensitized at 500°C (932°F) for 24 hours. For the welded specimens, the pipes were welded with a standard V-groove butt weld. The constant load tensile specimens were then machined transverse to the welds so that the pipe i.d. surface, including the weld and both heat affected zones, was located in the gage section.

The welded tensile specimen configuration is shown in Figure 20. The furnace-sensitized specimens were of similar configuration except for the absence of the butt weld. A load of 4.7 kN (1060 lb) was applied to the specimens after environmental specifications as described in Section 6.2.1 were achieved, the width of the cross-section being varied for each material to result in an applied stress equal to 136% of the 288°C (550°F) yield stress. The specimens were exposed in quadruplicate.

The only austenitic alloy which experienced IGSCC was a furnace-sensitized Type 304 specimen which cracked after 1530 hours of exposure to the 200 ppb oxygen environment. No materials cracked in the HWC environment. Although this result is not significant statistically, it does support other observations indicating that HWC mitigates the IGSCC phenomenon.

6.2.6 Martensitic Stainless Steel Bent Beam Tests

The objective of this brief task was to examine the effect of HWC and high oxygen (8 ppm) high purity water environments on the stress corrosion cracking (SCC) and hydrogen stress cracking (HSC) propensities of various wrought and cast high strength martensitic stainless steel alloys typically used in the BWR for pump shafts and impellers, valve trim, etc. The test materials included two wrought alloys (Type 410 stainless steel, 3 heat treatments and Type 422 stainless steel, 2 heat treatments) and two cast alloys (CA15 stainless steel, 2 heat treatments and CA6NM, 7 heat treatments).

The configuration of the bent beam specimens used in the tests is shown in Figure 21. The specimens were bent over a stainless steel fixture having a radius of curvature to give 1% strain in the outer fibers and were held at each end by carbon steel bolts. The specimens were removed from the autoclave at approximate total exposure times of 1, 2, 4, 8, and 16 months and examined for cracks (without removal from the fixture) using a stereo microscope at magnifications up to 40X.

The results of this scoping test program revealed that wrought martensitic stainless steels Types 410 and 422 and cast martensitic stainless steels CA15 and CA6NM, in several welded and non-welded, annealed, and tempered 593°C (1100°F) to 677°C (1250°F) conditions showed no evidence of cracking in 8 ppm oxygen 288°C (550°F) high purity water environment. These same alloys and heat treatment conditions also showed no evidence of cracking in a simulated HWC environment [high purity 288°C (550°F) water containing nominally 10 ppb oxygen and 230 ppb hydrogen]. Therefore, it appears that the presence of higher amounts of dissolved hydrogen in the coolant (~10X nominal) does not result in hydrogen stress cracking/hydrogen embrittlement in these materials over this test period.

6.3 CONCLUSIONS

These test results indicate the following conclusions concerning the effects of HWC on the general, crevice, galvanic and stress corrosion of BWR structural materials:

1. The corrosion rates and metal-to-system release rates are not significantly different for the two carbon steels and the two low alloy steels tested in HWC. However, the corrosion rates were significantly higher in HWC than in the nominal environment. Scratch defects in the oxide film of carbon and low alloy steels showed no significant effect on corrosion or metal-to-system release rates on exposure to HWC.

2. Types 304 and 316L stainless steel corrosion and metal release rates are very low in both HWC and reference 200 ppb O_2 water.

3. As anticipated, Alloy 600 corrosion rates are much faster than those for Types 304 and 316L stainless steel, but initial weight gains are lower. Corrosion rate and metal-to-system loss are lower in the HWC environment than in the nominal BWR environment for Alloy 600.

4. The initial carbon steel corrosion films are less protective in the HWC environment, resulting in up to 40 times higher corrosion rates than in the nominal environment and correspondingly higher metal-to-system loss. However, this acceleration in corrosion rate can be controlled in practice by injecting oxygen into the feedwater system.

5. Crevices appear to have no significant effect on corrosion rates or metal-to-system loss except for slightly reduced rates for Types 304 and 316L stainless steel.

6. Oxide film studies revealed that thinner films are formed on stainless steel in low O_2 environment while the films on carbon and low alloy steel are unaffected. Information derived from the injection of cobalt into the water indicated that low O_2 has no effect on the cobalt concentrations in the initial films formed on the steels.

7. SA106-B and SA333-6 carbon steels loaded to 190% of the 288°C (550°F) yield strength and SA333-6 and SA508-2 low alloy steels loaded to 110% of the 288°C (550°F) yield stress show no cracking after exposure for 5,359 hours in the HWC environment or up to 11,371 hours in reference 0.2 ppm O_2 water environment.

8. Types 304 and 316L stainless steel and Alloy 600 showed no evidence of cracking when stressed at constant load to 136% of the 288°C (550°F) yield strength for 5,359 hours in HWC environment. However, exposure to the nominal environment did result in cracking of one furnace-sensitized Type 304 stainless steel specimen after 1,530 hours.

9. Bent beam tests on martensitic stainless steel specimens indicated that excess hydrogen in the BWR environment does not induce any loss in ductility in high strength alloys. No cracking was observed in either the HWC or the control environment; the latter is in agreement with the excellent field performance of this family of alloys.

7.0 SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

Overall, the results of these laboratory and Dresden-2 HWC materials programs are highly encouraging. Hydrogen water chemistry clearly improves the stress corrosion cracking performance of several BWR structural materials as follows:

1. HWC prevents IGSCC of sensitized Type 304 stainless steel and Alloy 600 and TGSCC of low alloy and carbon steel.

2. HWC clearly provides mitigation of IGSCC in furnace sensitized Type 304 stainless steel and TGSCC of carbon steel and low alloy steel at Dresden-2. These results are in exact agreement with laboratory studies.

3. For pre-cracked furnace sensitized Type 304 stainless steel a Dresden-2 CERT test and preliminary DC potential drop studies indicated mitigation of crack propagation in-reactor. These results combined with laboratory pre-cracked pipe tests results and the ISI data at Dresden-2 indicate that pre-existing cracks at Dresden-2 should not propagate during HWC operation.

4. The ECPs of all the tested BWR structual materials decrease with decreasing oxygen content. During times when HWC is terminated, a "memory" effect occurs in that the potential of Type 304 stainless steel does not rapidly rise into a range (> -325 mV_{SHE}) where IGSCC can occur. This "safety" window of time appears to be ~10 hours.

4. HWC prevents initiation and propagation of IGSCC in welded Type 304 stainless steel piping at high stress levels (twice ASME Code allowable). A FOI of >25 has been achieved on crack initiation for full size Type 304 stainless steel piping in the HWC environment.

6. For Type 304 and Type 316 Nuclear Grade stainless steels, low alloy steel and carbon steel, no measurable crack growth is observed in HWC even at high stress intensities. Measurable crack growth is observed for Type 304 stainless steel and carbon steel in the normal BWR environment.

7. Cyclic crack propagation rates are significantly reduced in HWC for stainless, low alloy and carbon steel even at high stress intensities.

8. No detrimental effects such as hydrogen embrittlement have been found for high strength materials such as Alloy 600, Alloy X-750 and martensitic stainless steels in the HWC environment.

9. The general corrosion rates of Alloy 600 and stainless steel are reduced in the HWC environment, but there is an acceleration in general corrosion rates of carbon and low alloy steel. (This potential problem can readily be addressed, if deemed necessary, by oxygen injection into the feedwater system.)

The results obtained from in-reactor studies and from the laboratory tests conducted under this program correlate well, and it appears that the laboratory results are directly applicable for predicting materials behavior in Dresden-2.

All evidence available to date suggests that HWC has been effective in mitigating IGSCC during reactor power operation at the Dresden-2 station.

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Table 1

TEST MATRIX FOR HYDROGEN WATER CHEMISTRY PIPE TESTS

		Test Condition/Specimen Number		
	Heat	Normal BWR Water	Hydrogen Water Chemistry	
Material	Number	200 ppb O_2	50 ppb O_2	20 ppb O_2
Reference Specimens				
Type-304 SS	04836	AWC-5		
Type-304 SS	04836	AWC-6		
Type-304 SS	51416	AWC-7		
Type-304 SS	M2152	AWC-8		
Crack Growth Specimens				
Type-304 SS	04836	AWC-1 (Precrack) →	AWC-1	
Type-304 SS	04836	AWC-2 (Precrack)*		
Type-304 SS	04836	AWC-3 (Precrack) →	AWC-3 →	AWC-3
Type-304 SS	04836	AWC-4 (Precrack)*		
Type-304 SS	04836		AWC-9(Precrack) →	AWC-9
Type-304 SS	04836		AWC-10(Precrack) →	AWC-10
Type-304 SS	04836		AWC-11(Precrack) →	AWC-11
Type-304 SS	51416		AWC-12(Precrack) →	AWC-12
Type-304 SS	M2152		AWC-13(Precrack) →	AWC-13
**Type-304 SS	04836	AWC-15 (Precrack) →	→	AWC-15
**Type-304 SS	04836	AWC-16 (Precrack) → AWC-16 ←		
Crack Initiation Specimens				
Type-316 NG SS	03165		AWC-14 →	AWC-14
**Type-304 SS	04836		AWC-17	
**Type-304 SS	M1989		AWC-18	
**Type-304 SS	M2152		AWC-19	

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*For metallographic crack depth determination

**New tests

Table 2

ESPOSURES AND RESULTS OF HWC PIPE TESTS(1)

		200 PPB O_2 Water		50-70 PPB O_2 Water		20 PPB O_2 Water (HWC)	
Specimen Number	Heat Number	Hours Exposure	Maximum Depth, mm (mils)[2]	Hours Exposure	Maximum Depth, mm (mils)[2]	Hours Exposure	Maximum Depth, mm (mils)[2]
Reference Specimens							
AWC-5	04836	2044	Failed				
AWC-6	04836	1645	Failed				
AWC-7	51416	1059	Failed				
AWC-8	M2152	1339	Failed				
Crack Growth Specimens							
AWC-1	04836	308	0.38(15)[3]	844	Failed		
AWC-2	04836	308	1.40(55)[3]				
AWC-3	04836	1075	0.25(10)[3]	877	1.52(60)	3955	2.54(100)
AWC-4	04836	654	1.12(44)[3]				
AWC-9	04836			847	1.27(50)[3]	3974	2.67(105)[4]
AWC-10	04836			847	1.95(77)[3]	4115	1.95(77)
AWC-11	04836			848	1.42(56)[3]	3082	1.42(56)
AWC-12	51416			847	2.54(100)[3]	3911	>5.08(>200)
AWC-13	M2152			848	>5.08 (>200)[3]	3082	>5.08(>200)
AWC-15	04836	343	1.27(50)[3]			5310	(5)
AWC-16	04836	343	1.02(40)[3]				
		1285	Failed				
Crack Initiation Specimens							
AWC-14	03165			847	No Cracks[4]	4047	No Cracks (UT)
AWC-17	04836					5122	No Cracks (UT)
AWC-18	M1989					7580	No Cracks (UT)
AWC-19	M2152					7585	No Cracks (UT)

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(1) All except AWC-14 are Type-304 stainless steel. AWC-14 is Type-316 NG stainless steel.
(2) As estimated by UT inspection unless noted otherwise.
(3) Precrack depth.
(4) Measured on metallographic section.
(5) UT complete, metallography to measure crack growth.

Table 3

SCC CRACK GROWTH TEST RESULTS IN HWC

HWC (20 ± 15 ppb O_2, 125 ± 25 ppb H_2, <0.2 μS/cm)

Material	Growth Rate	Stress Intensity
FS*Type 304	No Growth**	$K \leq 31.2$ MPa $\sqrt{m}$ (28.4 ksi $\sqrt{in.}$)
FS Type 316 NG	No Growth	$K \leq 30.1$ MPa $\sqrt{m}$ (27.4 ksi $\sqrt{in.}$)
SA508	No Growth	$K \leq 50.9$ MPa $\sqrt{m}$ (46.3 ksi $\sqrt{in.}$)
SA333-6	No Growth	$K \leq 44.8$ MPa $\sqrt{m}$ (40.3 ksi $\sqrt{in.}$)

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* FS = Furnace sensitized 621°C (1150°F/12h)

** Below detectable limit, i.e., growth rate $<8 \times 10^{-8}$ mm/s (3×10^{-9} in./s).

Table 4

SCC CRACK GROWTH TEST RESULTS IN 200 PPB OXYGEN WATER

Material	Growth Rate	Stress Intensity
FS Type 304	8.9×10^{-8} mm (3.5×10^{-9} in.)/s	$K = 17.3$ MPa $\sqrt{m}$ (15.7 ksi $\sqrt{in.}$)
FS Type 316 NG	No Growth	$K \leq 26.7$ MPa $\sqrt{m}$ (24.3 ksi $\sqrt{in.}$)
SA 508	Incipient Growth	$K = 49.1$ MPa $\sqrt{m}$ (44.7 ksi $\sqrt{in.}$)
SA 106-B	1.4×10^{-7} mm (5.2×10^{-9} in.)/s	$K = 44.0$ MPa $\sqrt{m}$ (40.0 ksi $\sqrt{in.}$)

Table 5. FATIGUE CRACK GROWTH TEST RESULTS*

Material	Cyclic Frequency, cph	Environment	Stress Intensity $\mathrm{MPa}\sqrt{\mathrm{m}}$ ($\mathrm{KSI}\sqrt{\mathrm{in}}$)	Crack Growth Rate mm/cycle $\times 10^{-5}$	(in/cycle) ($\times 10^{-5}$)	Factor of Improvement
S Type 304	0.74	HWC	30.9 (28.1)	69	(2.7)	3
		200 ppb O_2	30.3 (27.6)	254	(10)	--
	7.5	HWC	25.8 (23.5)	16	(0.63)	3
		200 ppb O_2	36.5 (33.2)	50	(2.0)	--
SA 508-2	0.74	HWC	34.1 (31.0)	7.6	(0.3)	7
		200 ppb O_2	37.6 (34.2)	50.8	(2.0)	--
	7.5	HWC	33.8 (30.8)	1.7	(0.07)	450
		200 ppb O_2	33.7 (30.7)	760	(30)	--
SA 333-6	0.74	HWC	30.4 (27.7)	5.6	(0.22)	20
		200 ppb O_2	30.6 (27.8)	109	(4.3)	--
	7.5	HWC	24.2 (22.0)	0.33	(0.013)	1000
		200 ppb O_2	23.7 (21.6)	330	(13)	--

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*Since there is no control data for Type 316NG stainless steel, no comparison could be made.

Table 6

CONCENTRATION OF GASES

Gas Phase (Pressurized Tanks)		Aqueous Phase	
O_2	H_2	O_2	H_2
%		ppb (calculated)	
2.5	0	1000	0
0.50	0	200	0
0.50	6.5	200	102
0.125	0	50	0
0.125	7.7	50	120
0.09		36	
0.08	7.7	32	120

Table 7

CERT RESULTS FOR MATERIALS TESTED IN HIGH PURITY WATER AT 274°C (525°F)

Material and Condition	Dissolved Gases (ppb) Inlet O_2	Inlet H_2*	Effluent O_2	Effluent H_2*	Fracture Stress(1) MPa	Fracture Stress(1) ksi	UTS(2) MPa	UTS(2) ksi	T_f(3) (h)	R.A.(4) (%)	Elongation (%)	Fracture Morphology
T-304SS, W	200	0	180	0	610	88.6	429	62.2	246	29.8	29.2	20% IGSCC; 80% Ductile
T-304SS, W+LTS	200	0	180	0	600	87.1	409	59.3	244	31.5	26.8	30% IGSCC; 70% Ductile
T-304SS, W+LTS	200	100	100	100	694	100.7	403	58.5	236	41.9	27.1	25% IGSCC,**75% Ductile
T-304SS, W+LTS	45	112	19	112	1570	228	409	59.3	294	74	36.3	Ductile
SA533B	210	0	205	0	895	129.9	601	87.3	150	32.8	17.2	16% TGSCC; 84% Ductile Shallow pits, deep auxiliary cracks
SA533B	200	100	65	100	1700	246.7	637	92.5	203	62.8	21.9	100% Ductile
SA533B	45	112	13	112	1699	246.6	623	90.4	188	63.3	24.4	100% Ductile;minor pits
A 600, W+LTS	187	0	180	0	1072	155.6	559	81.1	362	47.9	42.8	100% Ductile
A 600, W+LTS	30	125	10	125	1103	160.1	525	76.2	342	52.4	40.7	100% Ductile
SA333 Grade 6	40	125	5	125	1076	156.2	471	68.4	262	56.2	29.6	100% Ductile

---

(1) Maximum load/failure cross section
(2) Maximum load/original cross section
(3) Failure time in hours
(4) Reduction in area

* H_2 concentration calculated for gas input

** 5% TGSCC also noted

W = Welded

LTS = Low Temperature Sensitized [500°C (932°F)/24 h]

Table 8

LABORATORY CERT TEST RESULTS IN LOW OXYGEN WATER

Spec I.D.	Material	Strain Rate (min^{-1})	Time to Failure (h)	Max. Stress MPa (ksi)	RA (%)	Elongation (%)	Fracture Mode
A106-1	SA106B(1) Carbon Steel	1×10^{-4}	46	496 (72.0)	41.6	28.6	100% Ductile
A106-2	SA106B(2) Carbon Steel	1×10^{-4}	39.5	494 (71.7)	35.6	26.3	100% Ductile
A533-1	SA533B Cl I(1) Low Alloy Steel	1×10^{-4}	47	571 (82.8)	70.4	32.0	100% Ductile
A508-1	SA508 Cl II(1) Low Alloy Steel	1×10^{-4}	43.5	581 (84.3)	75.0	28.6	100% Ductile

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Notes: * 50 ppb O_2, 230 ppb H_2, < 1 µS/cm conductivity at 288°C (550°F)

(1) Specimen was creviced by wrapping and spot welding thin stainless steel shim stock around the 3.1 mm (1/8 in.) diameter test section.

(2) This specimen was tested without a crevice.

Table 9

SET TEST MATRIX IN 0.01N Na_2SO_4 AT 274°C
UNDER POTENTIAL CONTROL, STRAIN RATE 2×10^{-5} min^{-1}

	Controlled Potentials V_{SHE}
Type 304 SS, welded + LTS* (500°C/24 hours)	-0.100, -0.500
Alloy 600, welded + LTS (500°C/24 hours)	-0.100, -0.500
Alloy X-750, three-step heat treated (1038°C/1 hour, 900°C/24 hours, 704°C/20 hours)	-0.100, -0.700

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*Low Temperature sensitized

Table 10

SET RESULTS IN 0.01N Na_2SO_4 AT 274°C (525°F)
(STRAIN RATE 2 x 10^{-5}/MIN)

Material and Metallurgical Condition	Electro-Chemical Potential	Fracture Stress(1)		UTS(2)		T_f(3) (h)	R. A.(4) (%)	Elongation (%)	Fracture Morphology
		ksi	MPa	ksi	MPa				
Type-304SS, W+LTS	-0.100	35.1	242	33.7	232	36	3.9	4.8	100% IGSCC
Type-304SS, W+LTS	-0.500	178.3	1228	68.3	471	277	61.1	36.4	>95% Ductile, some TGSCC initiation
Alloy 600 W+LTS	-0.100	111.3	767	77.3	533	233.5	30.6	31.1	70% IGSCC, 30% Ductile
Alloy 600 W+LTS	-0.500	180	1240	83.2	573	320	53.8	43.3	100% Ductile
Alloy X-750 3-step heat treated	-0.100	275	1895	168.5	1161	306	39.1	31.2	100% Ductile
Alloy X-750 3-step heat treated	-0.700	258.4	1780	165.4	1140	283	36.0	31.5	100% Ductile

---

(1) Maximum load/failure cross section
(2) Maximum load/original cross section
(3) Failure time in hours
(4) Reduction in area

TABLE 11

ECP MEASUREMENTS AT DRESDEN NPS

10/83 THROUGH 4/84

- TOTAL TIME MEASURING ELECTROCHEMICAL POTENTIALS = 3330 HOURS (139 DAYS)
- TIME MEASURING ECPS WITH HWC OPERATING = 3160 HOURS
- HWC NOT OPERATING DURING ECP MEASUREMENTS = 170 HOURS (95% EFFICIENCY)

AVERAGE ECP MEASUREMENTS

	V_{SHE}	
	304 SS	PT
HWC WITH HYDROGEN ON	-0.430	-0.690
HWC WITH HYDROGEN OFF	-0.300(1)	-0.010
NORMAL BWR	-0.200(1)	

(1) ECP OF 304 SS DURING NORMAL HIGH OXYGEN CONDITIONS > -0.200 V (SHE). "MEMORY" EFFECT OF RECENT HWC OPERATION DECREASES OBSERVED VALUE

Table 12

Range of Electrochemical Potential and Oxygen in Hydrogen Water Chemistry, Nov. 19 to Dec. 18, 1983 at $273\pm2^{\circ}$C

Dissolved Oxygen (ppb)	Conductivity (μS/cm)	Potentials Volts (SHE)				
		304 SS	304 SS (filmed)	Gold	Platinum	Autoclave
30 to 6	0.16 to 0.11*	-0.40 to -0.46	-0.44 to -0.53	-0.52 to -0.62	-0.69 to -0.73	-0.39 to -0.46

* 0.29 μS/cm transient on 12/2

Table 13

Results of Dresden-2 and Laboratory HWC CERT Tests

	Material	Test Location	O_2 (ppb)	K[1] (uS/cm)	Time To Failure (h)	Time Off HWC (h)	Elongation %	Result
1)	FS[2] T-304	D-2	268	0.29	108	0	12	70% IGSCC
2)	FS T-304	D-2	40	0.37	143	2	20	35% IGSCC
3)	FS T-304	D-2	<20	0.29	>297	4	38	DF[3]
4)	FS T-304	D-2	5-20	0.19	208[4]	5	NM[5]	DF
5)	FS T-304	D-2	5-23	0.17	181	15	NM	Minor IGSCC along gauge
6)	FS T-304	D-2	3-30	0.13	396	36	45	DF
7)	FS T-304	D-2	7-19	0.09	400	25	46	DF
8)	FS T-304PC[6]	D-2	12-20	0.09	301[7]	7	40	No IGSCC Extension
9)	FS T-304	VNC[8]	195	<0.1	156	NA[9]	17	85% IGSCC
10)	FS T-304	VNC	15	<0.1	262	0	NA	DF
11)	SA 533B	D-2	150-280	0.29	37[10]	NA	12	40% TGSCC
12)	SA 533B	D-2	5-20	0.29	63	0	24	DF
13)	SA 533B	VNC	200	<0.1	43	NA	11	40% TGSCC
14)	SA 533B	VNC	12	<0.1	60	0	22	DF
15)	SA 508-2	D-2	12-18	0.08	52[11]	0	NM	DF
16)	SA 508-2[12]	VNC	50	<1	44	0	29	DF
17)	SA 106B	D-2	8-14	0.12	94	2	NA	DF
18)	SA 106B	VNC	50	<1	40	0	29	DF

1) K = Conductivity
2) FS = Furnace Sensitized 621°C (1150°F)/24 hr
3) DF = Ductile Fracture
4) Thermal Overload Ended Test
5) NM = Not Measured to Date
6) PC = Precracked in 200 ppb O_2
7) Plus 67 Hours Precracking (368 hr total)
8) VNC = Vallecitos Nuclear Center
9) Not Applicable, i.e., not a HWC Test
10) Extension rate was 3 mils/h for SA 533, SA 508-2, SA 106B and 1 mil/h for Type 304 Stainless Steel
11) Motor Failure, Specimen Fractured Manually
12) Creviced

Table 14

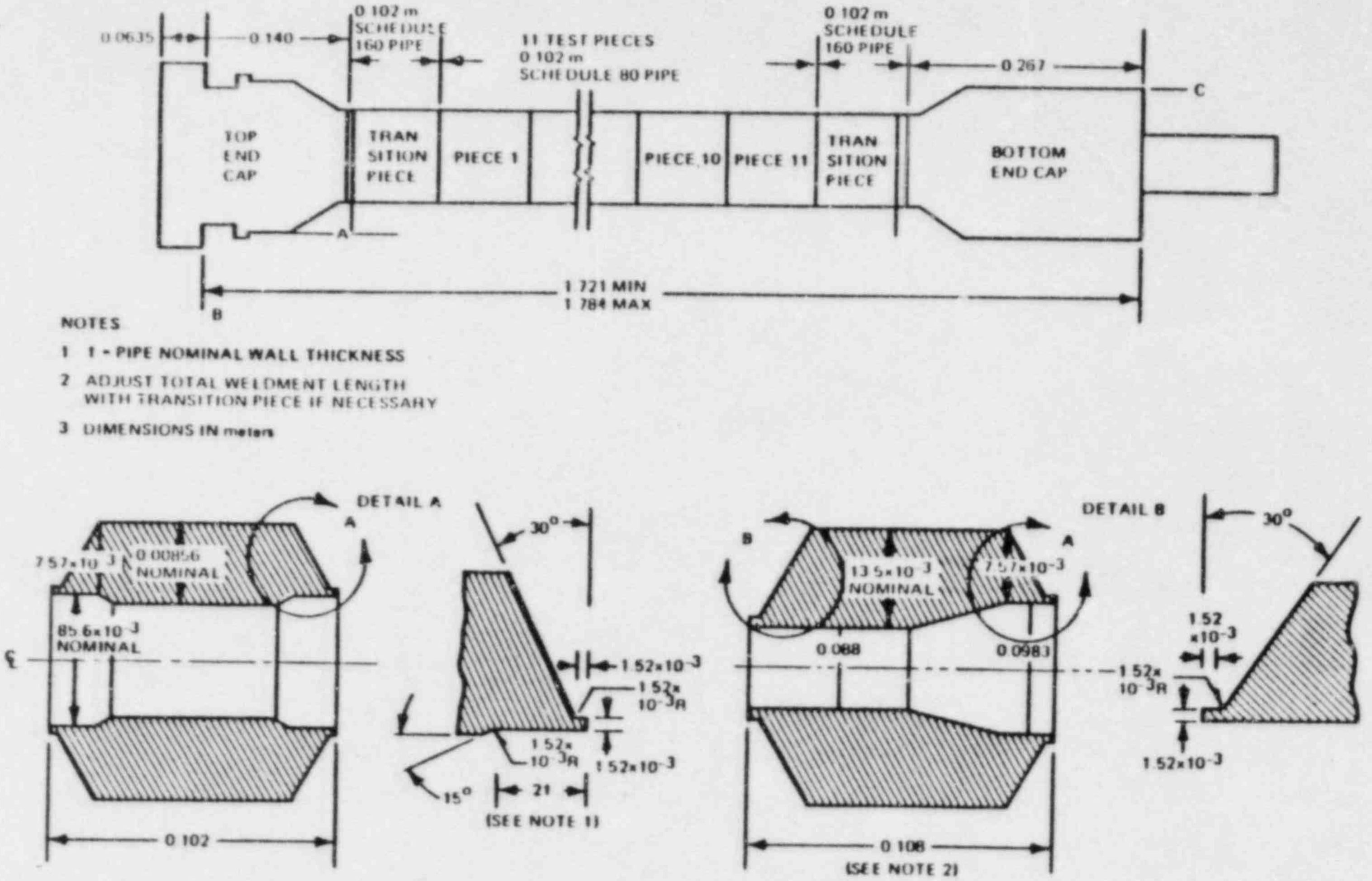
Mid-Cycle ISI Results from Dresden-2

ISI RESULTS

Weld	Date April 29, 1983	 November 12, 1983
28" Safe End PS2-201-1	1" long, 16% deep[1]	1" long, 13% deep
12" Riser (Two Cracks) PD5-D20	0.25" long, 17% deep 0.25" long, 19% deep	0.25" long, 15% deep 0.25" long, 17% deep
12" Riser (Two Cracks) PD5-D5	0.50" long, 19% deep 0.25" long, 14% deep	0.50" long, 18% deep 0.25" long, 16% deep

---

[1] Percentage Through Wall



NOTES

1. 1 - PIPE NOMINAL WALL THICKNESS
2. ADJUST TOTAL WELDMENT LENGTH WITH TRANSITION PIECE IF NECESSARY
3. DIMENSIONS IN meters

Figure 1. Pipe Test Specimen Fabrication Drawing

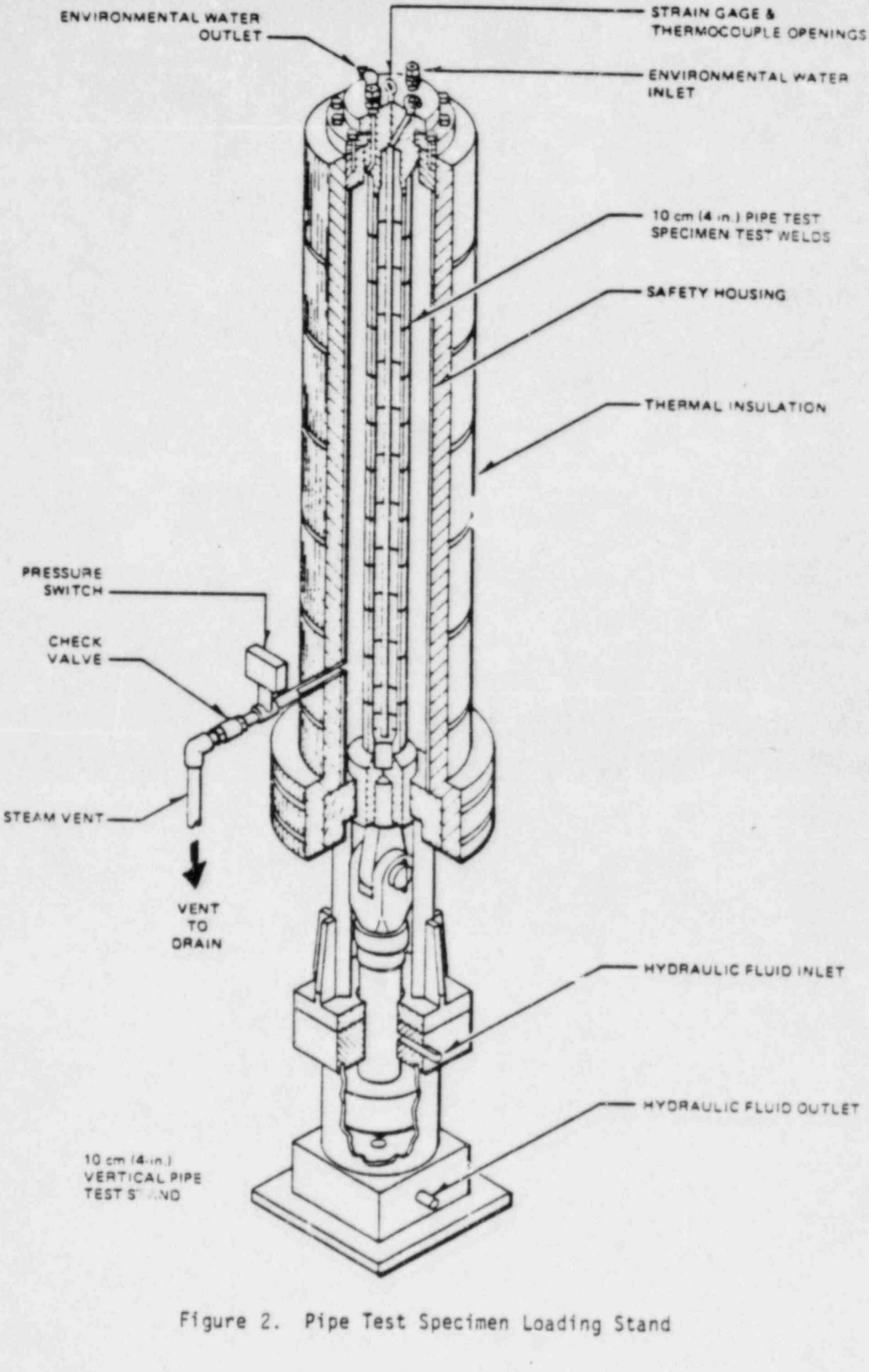


Figure 2. Pipe Test Specimen Loading Stand

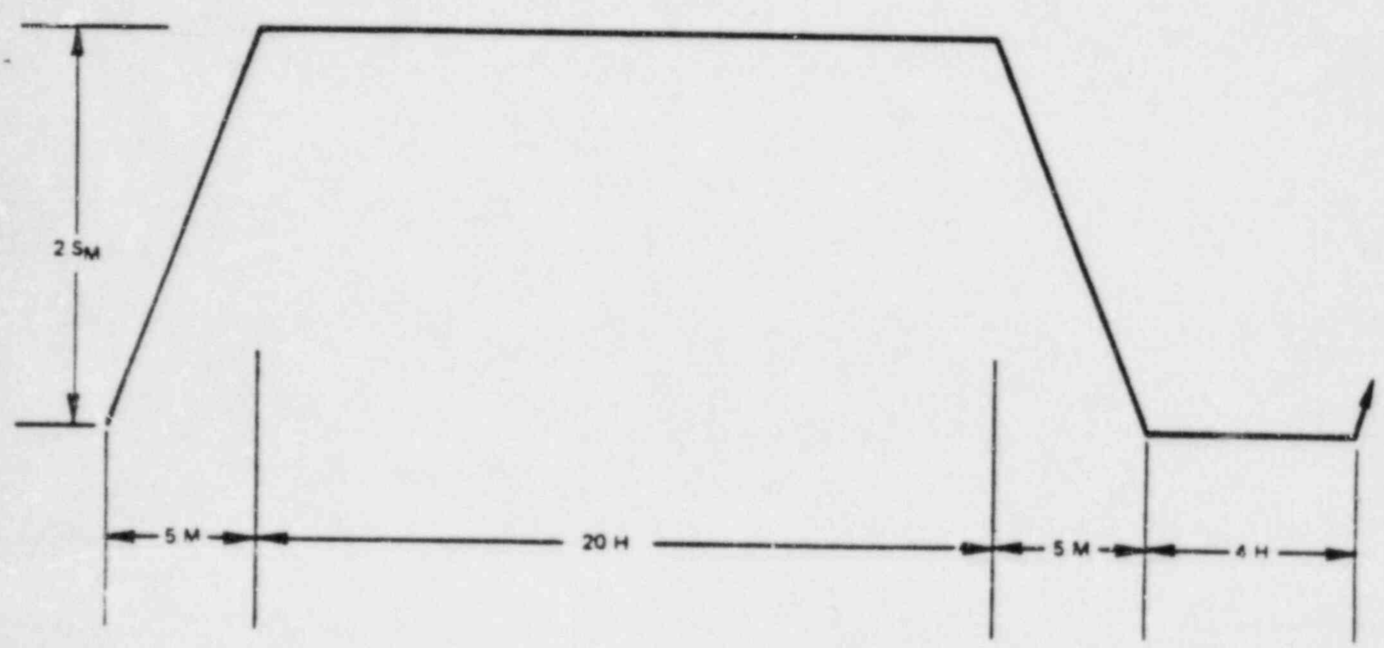


Figure 3. Loading Waveform used for Hydrogen Water Chemistry Pipe Tests. (M = minutes, H = hours, S_M = ASME Code Allowable Stress)

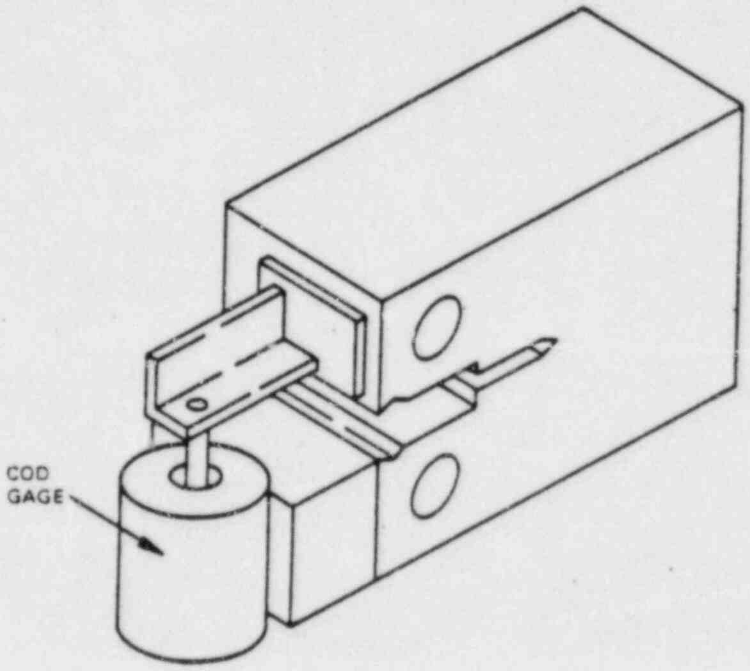


Figure 4. Typical WOL or Compact Tension Specimen for Crack Growth Rate Study

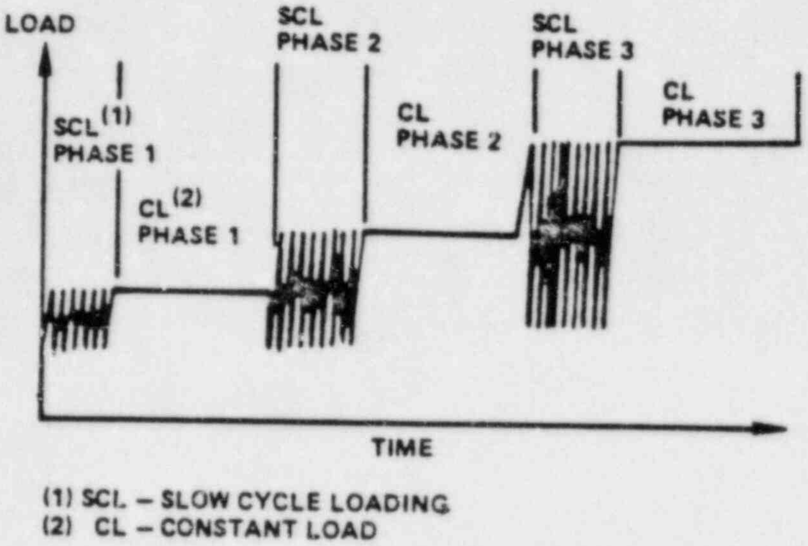


Figure 5a. Stress Corrosion Test Loading History

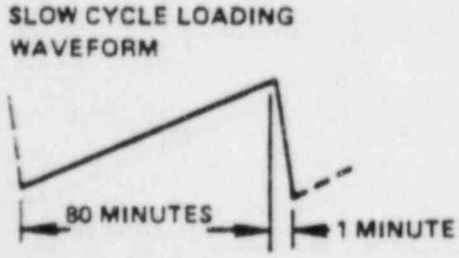


Figure 5b. Slow Cyclic Loading Waveform Detail

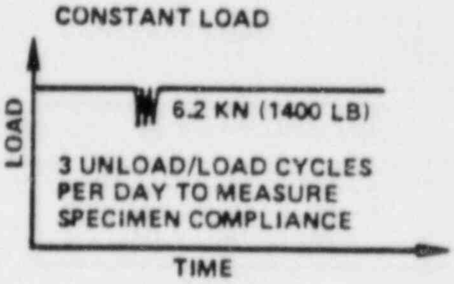


Figure 5c. Constant Load Detail

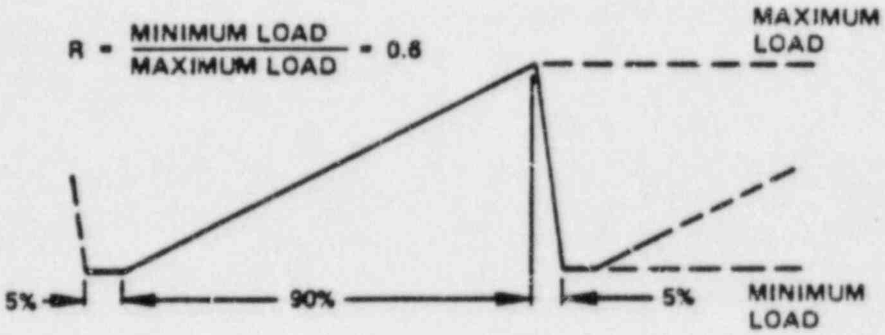


Figure 6. Cyclic Loading Waveform

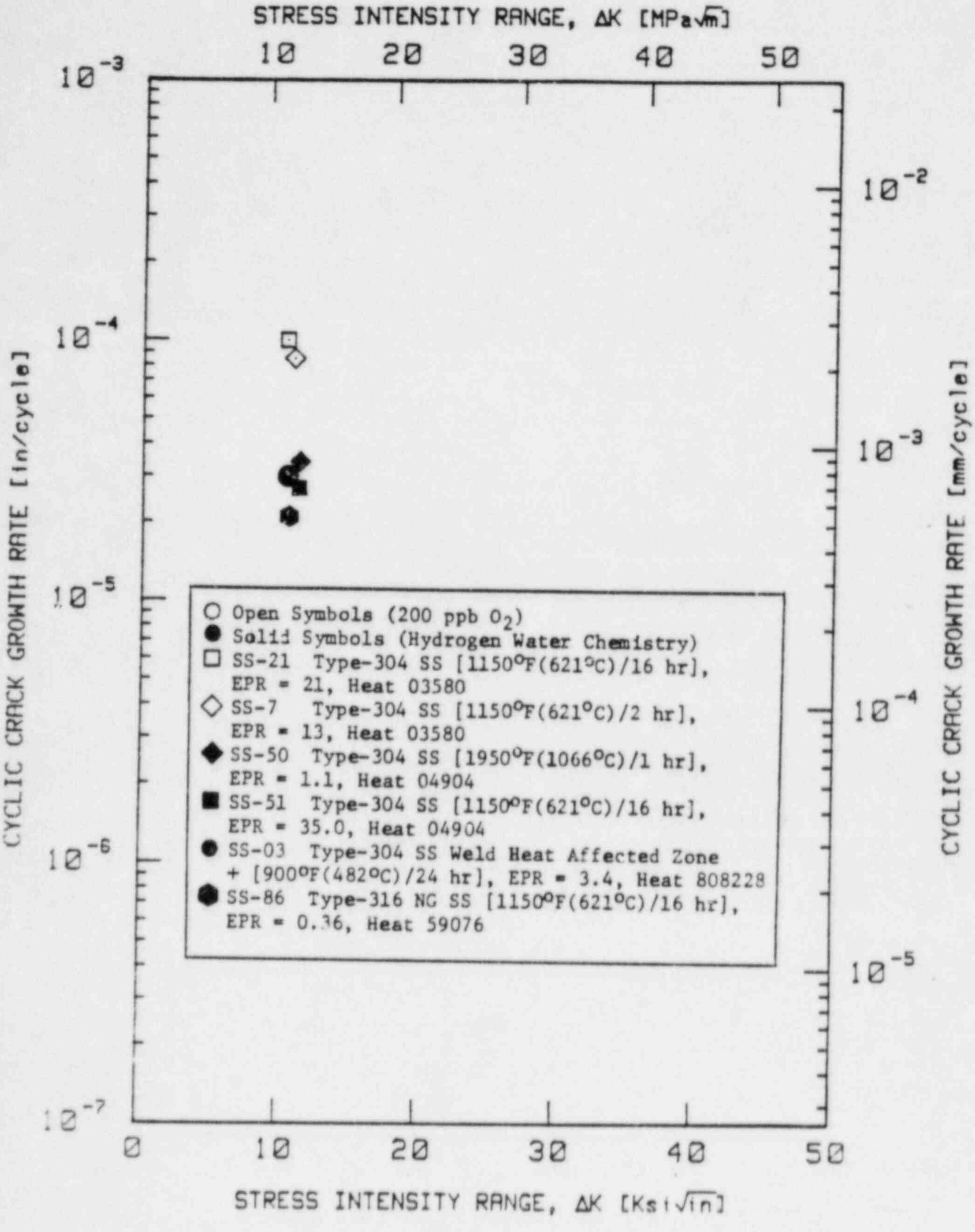


Figure 7. Comparison of Cyclic Crack Growth Data (0.74 cph, R=0.6) in HWC versus Normal Environment for Furnace Sensitized Stainless Steel

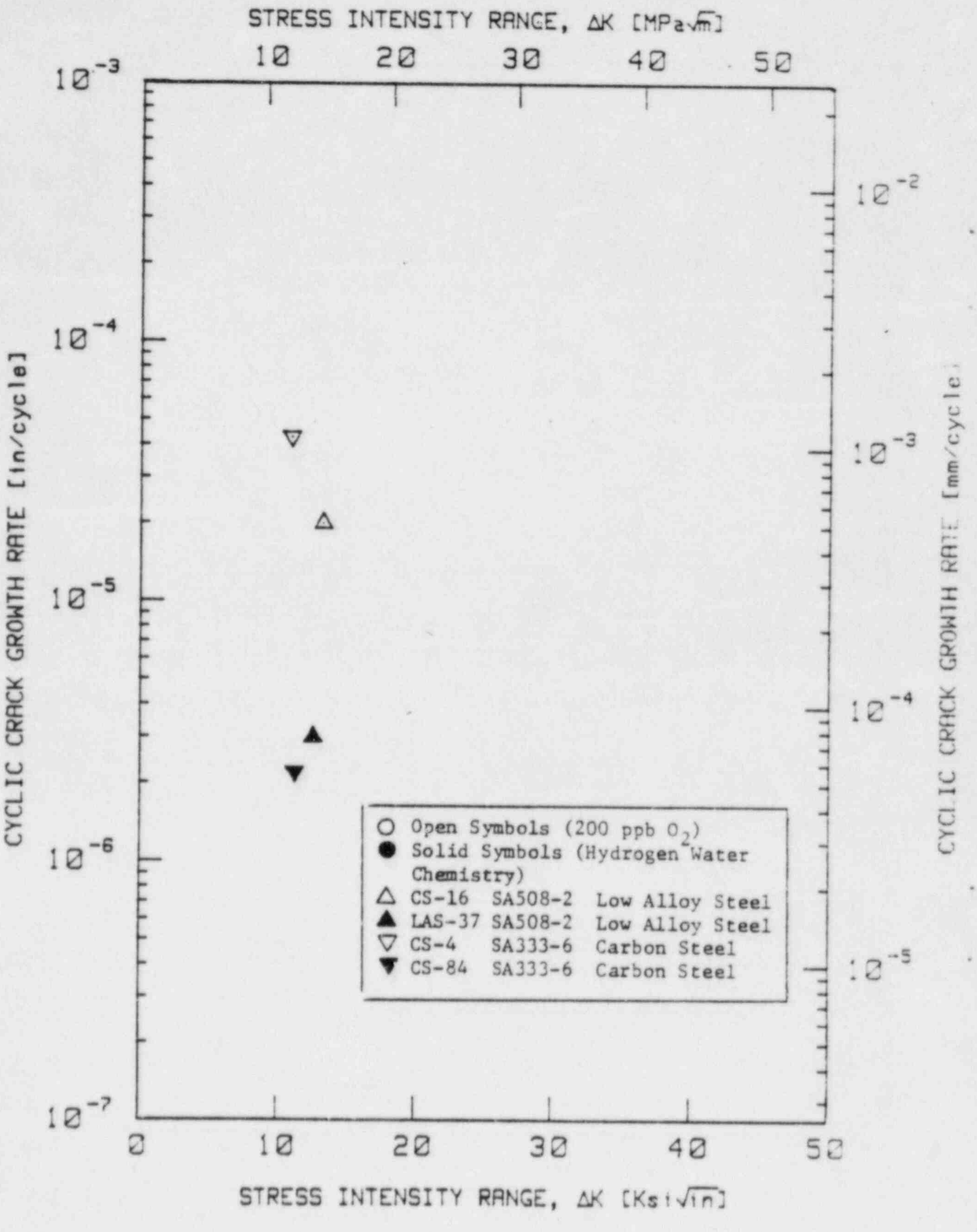


Figure 8. Comparison of Cyclic Crack Growth Data (0.74 cph, R=0.6) in HWC versus Nominal Environment for Carbon and Low Alloy Steel

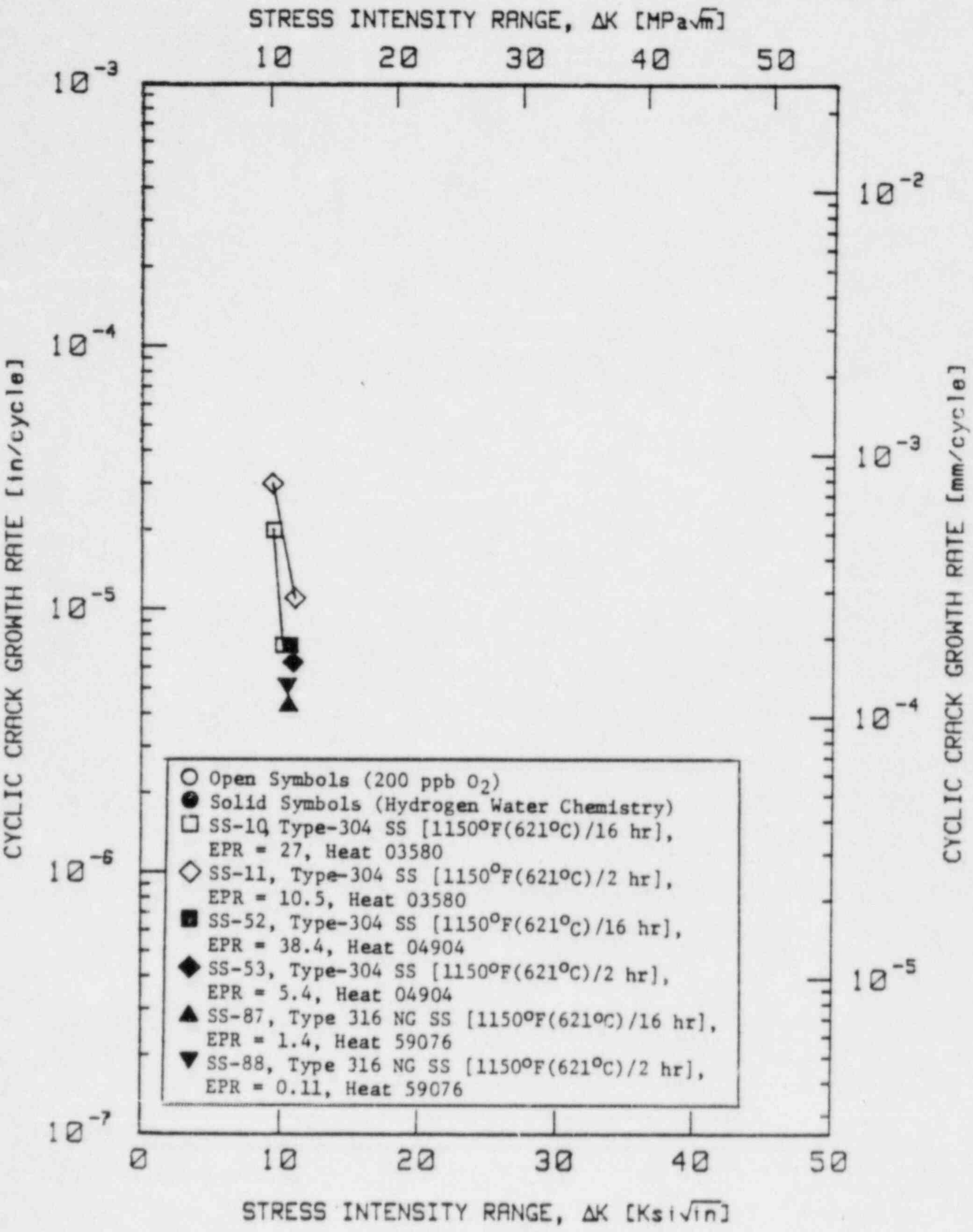


Figure 9. Comparison of Cyclic Crack Growth Data (7.5 cph, R=0.6) in HWC versus Nominal Environment for Furnace Sensitized Stainless Steel

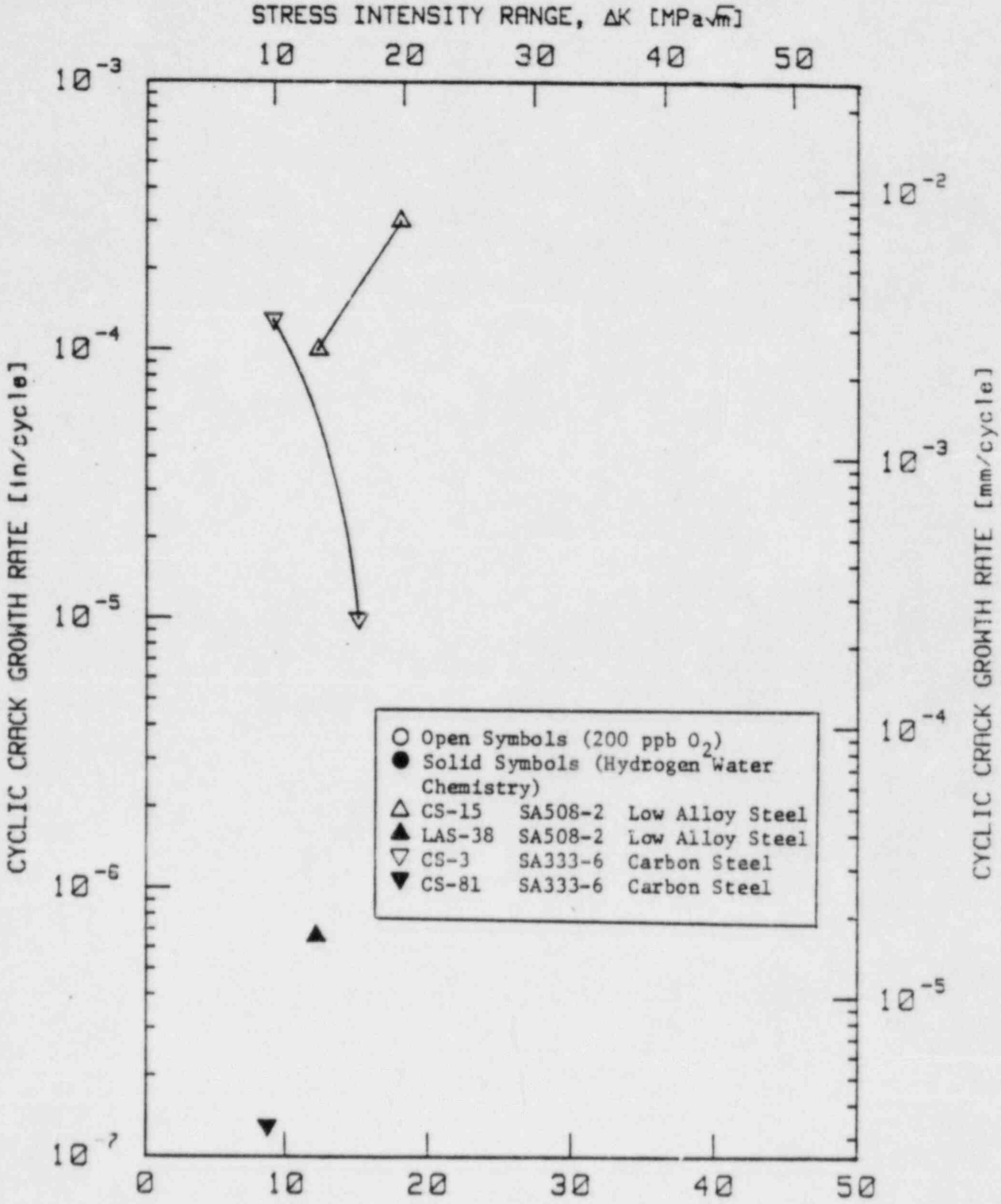


Figure 10. Comparison of Cyclic Crack Growth Data (7.5 cph, R=0.6) in HWC versus Nominal Environment for Carbon and Low Alloy Steel

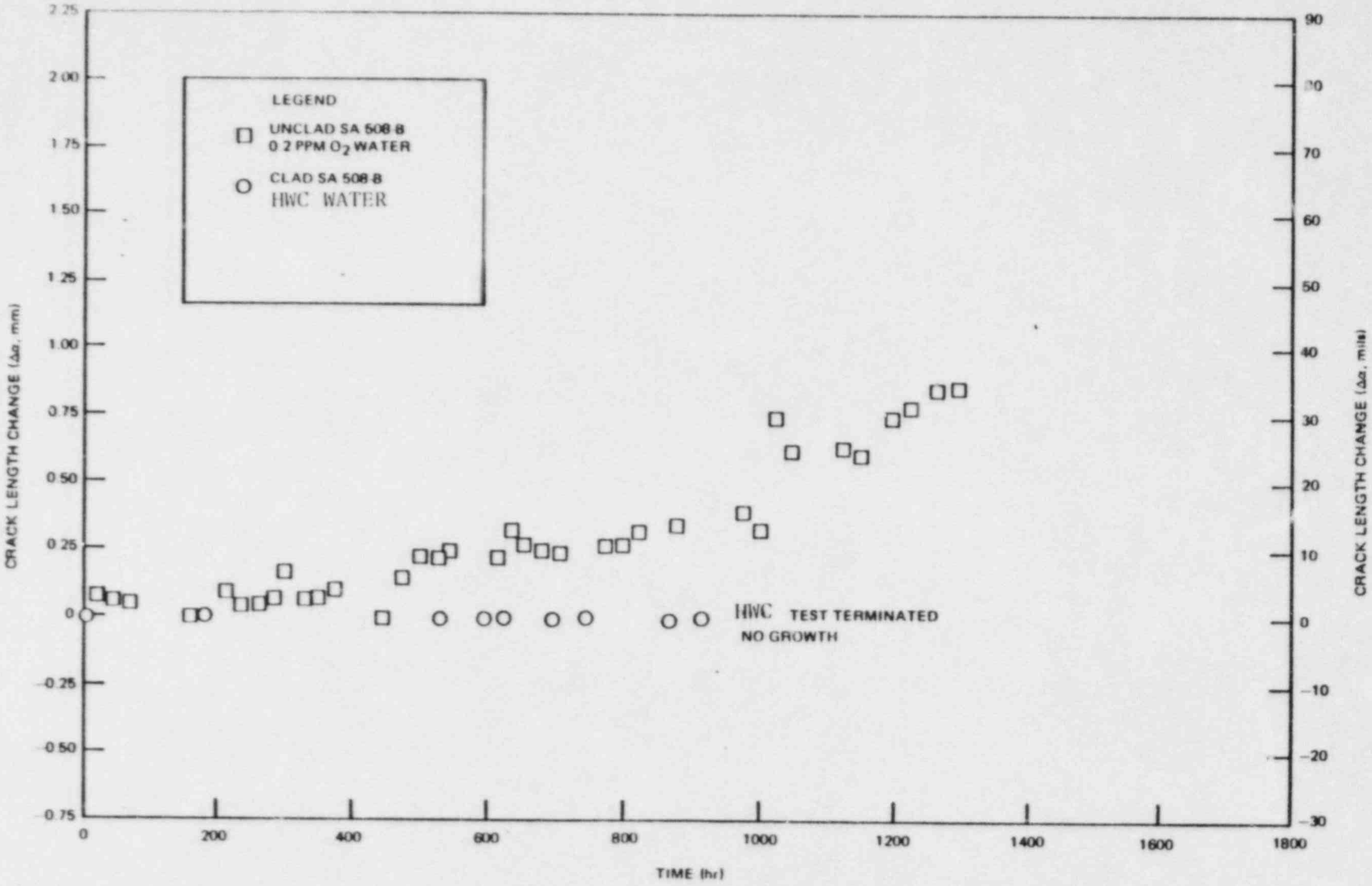


Figure 11. Crack Growth Data Slow Rising Load, SA508-2

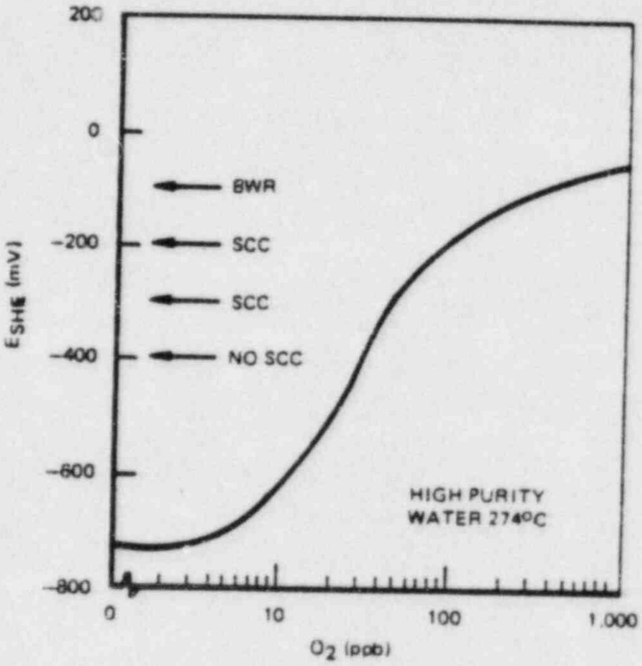


Figure 12. Relationship Between Dissolved Oxygen and Potential to IGSCC of Welded Type 304 Stainless Steel

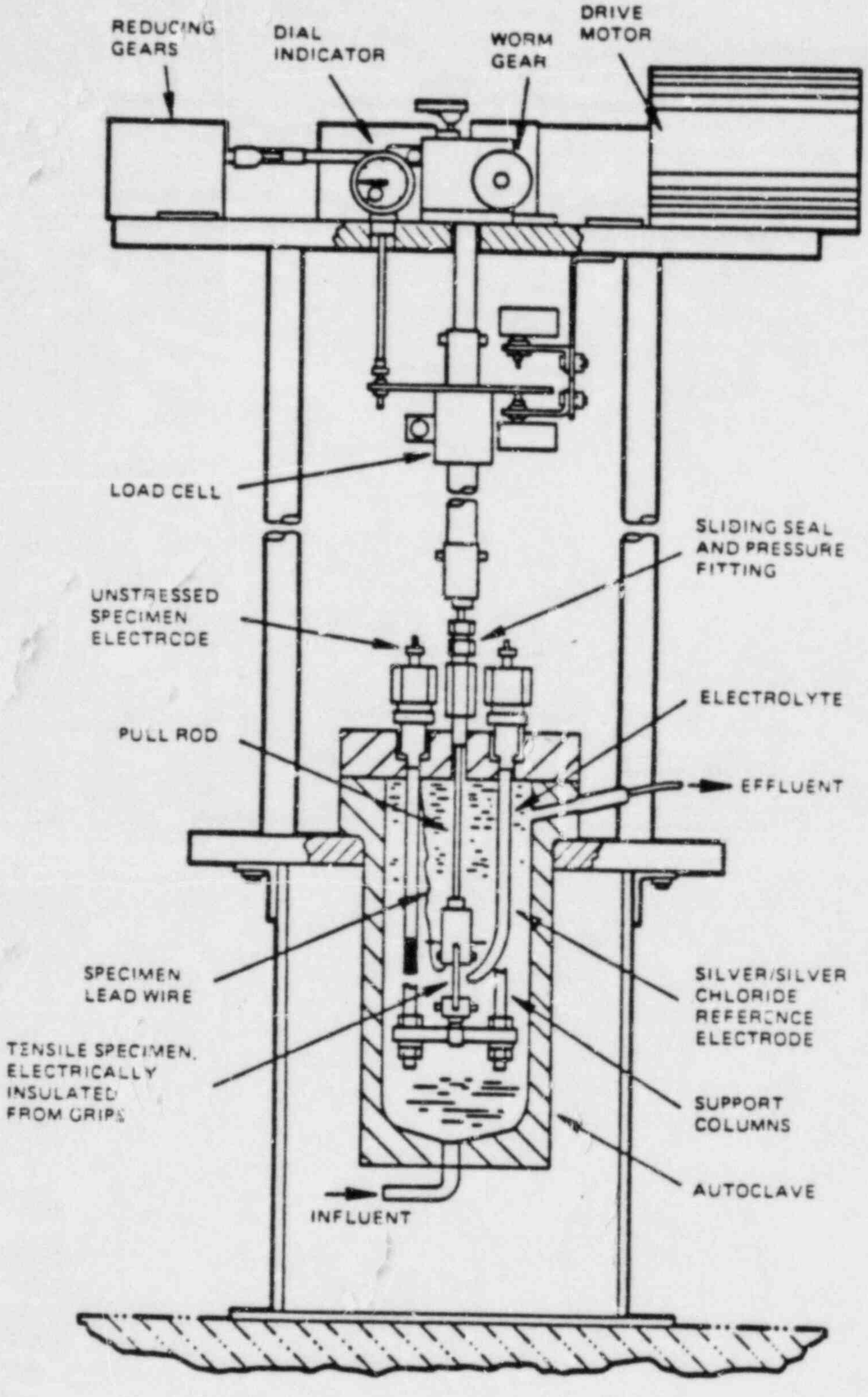


Figure 13. SET Facility

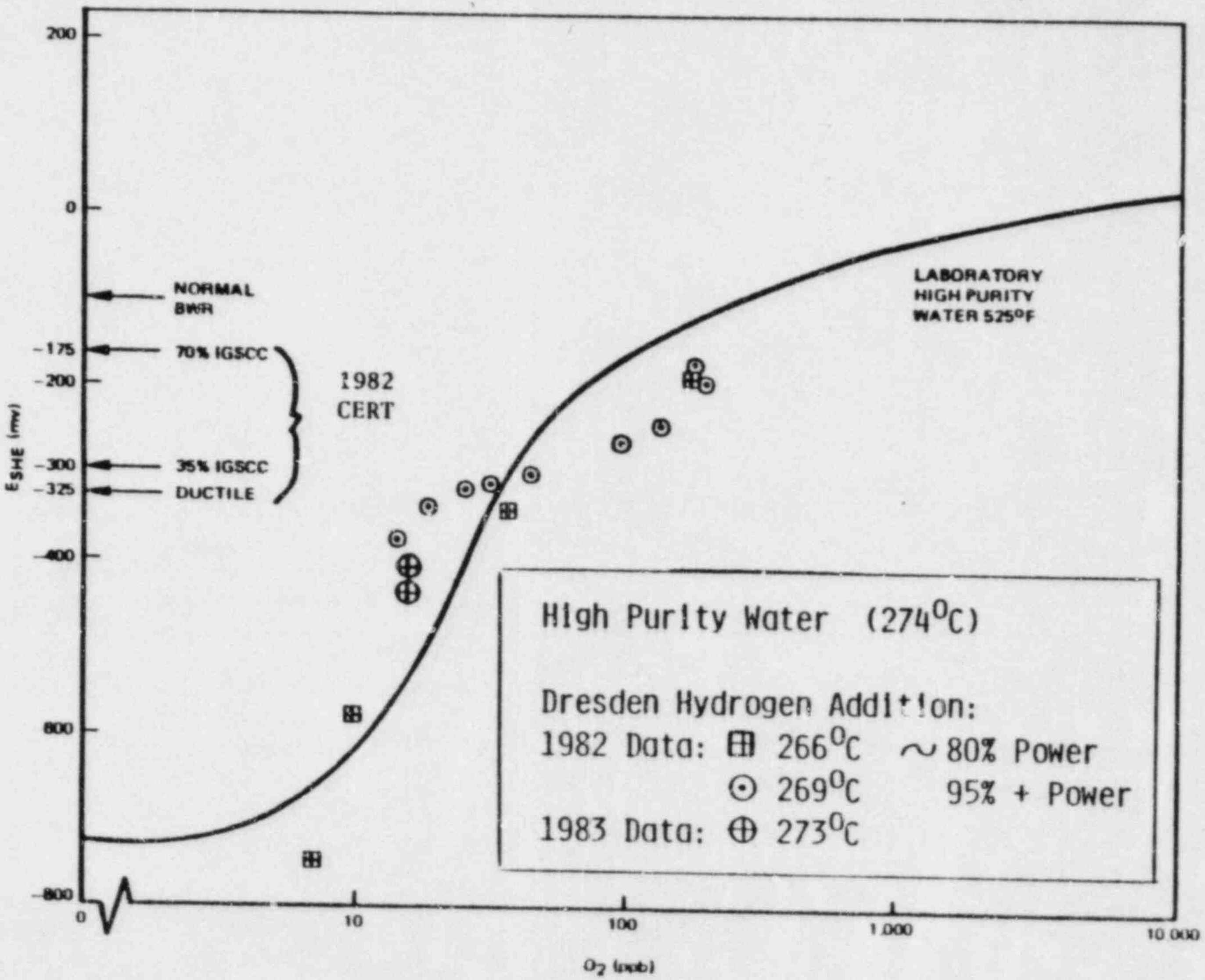


Figure 14. The Effect of Dissolved Oxygen on the Corrosion Potential of Type 304 Stainless Steel in High Purity Water at 274°C (525°F)

Figure 15. Example of ECP Memory Effect During H_2WC

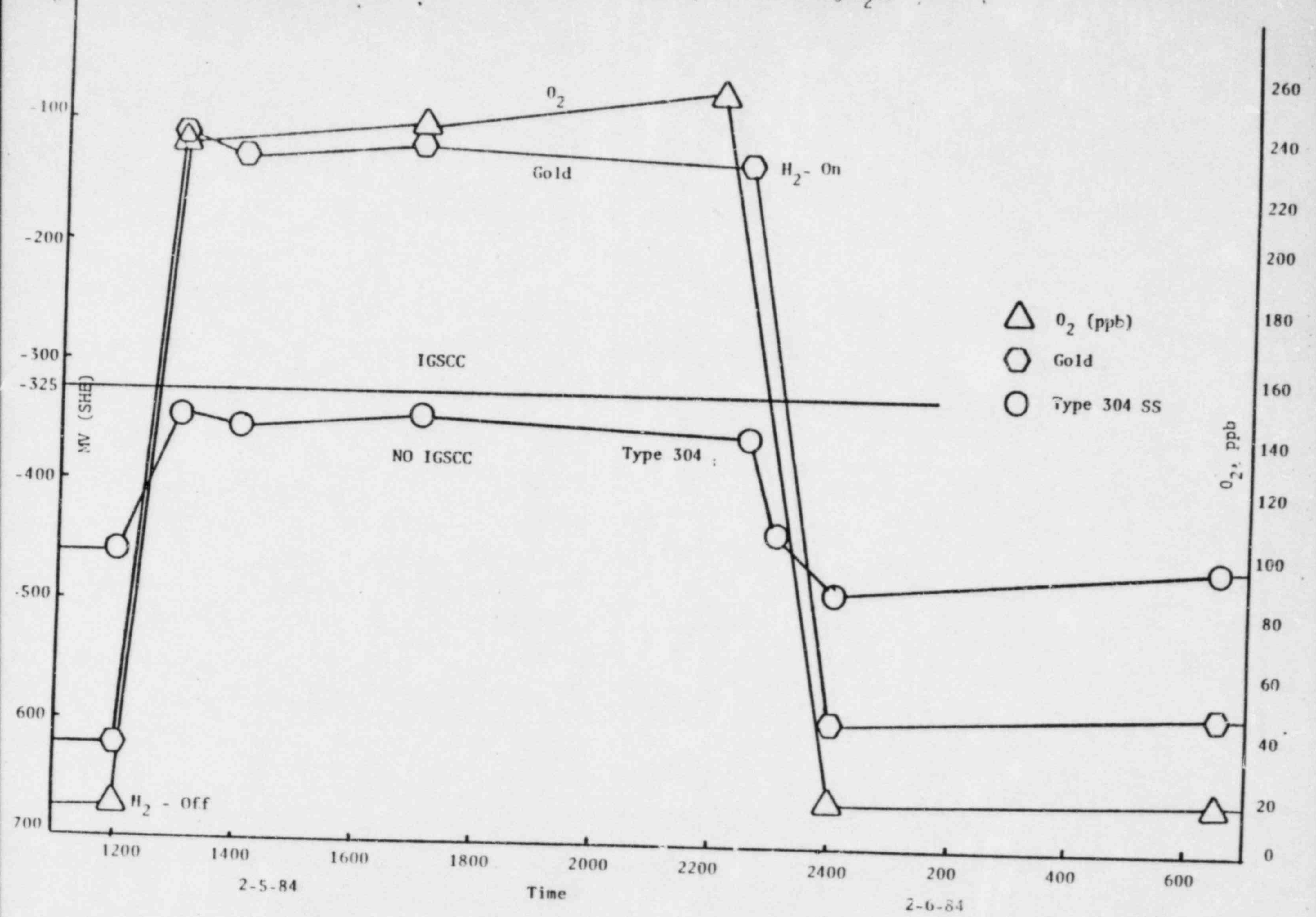


Figure 16. IGSCC BEHAVIOR OF SENSITIZED STAINLESS STEEL IN DRESDEN-2 TESTS

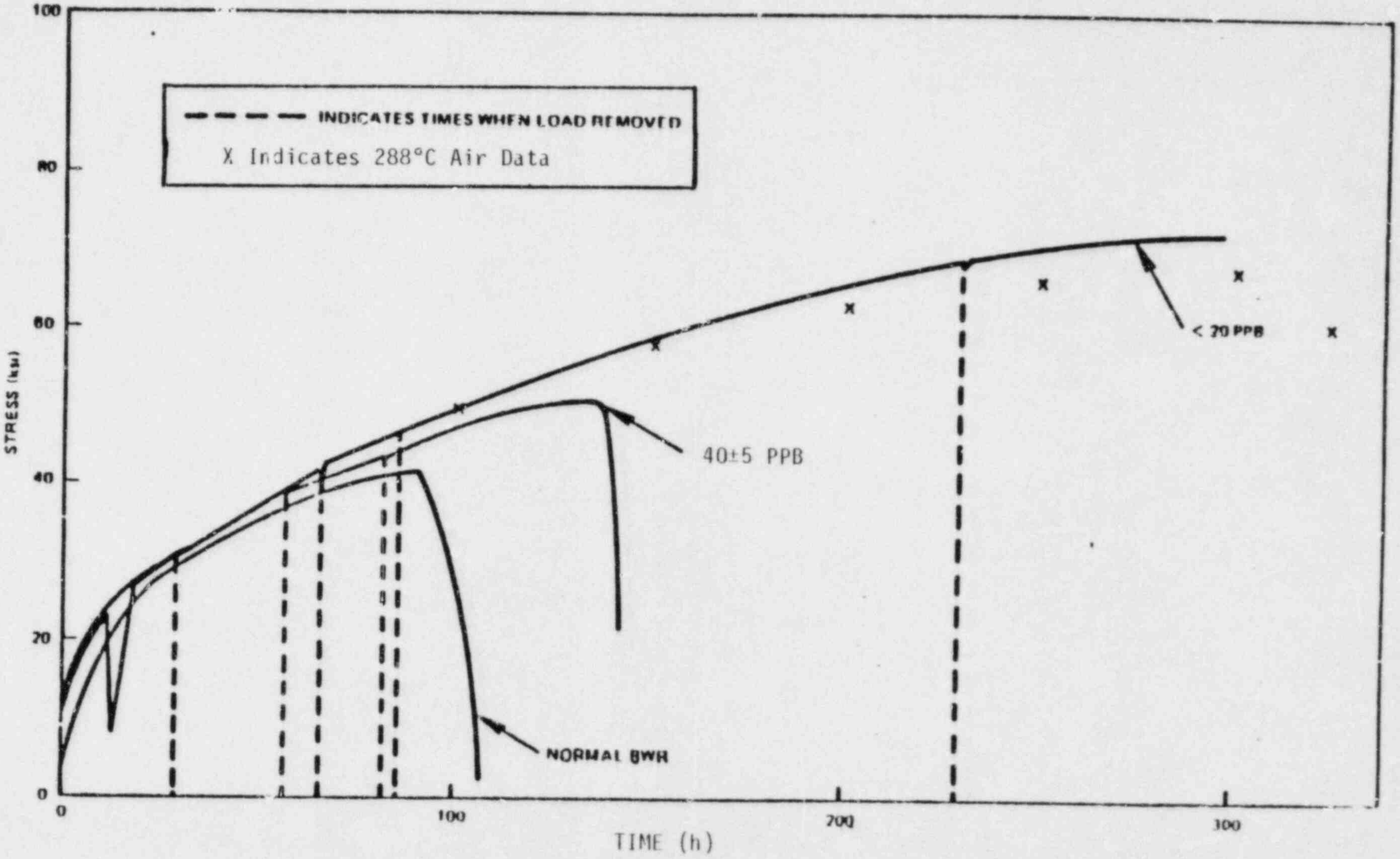
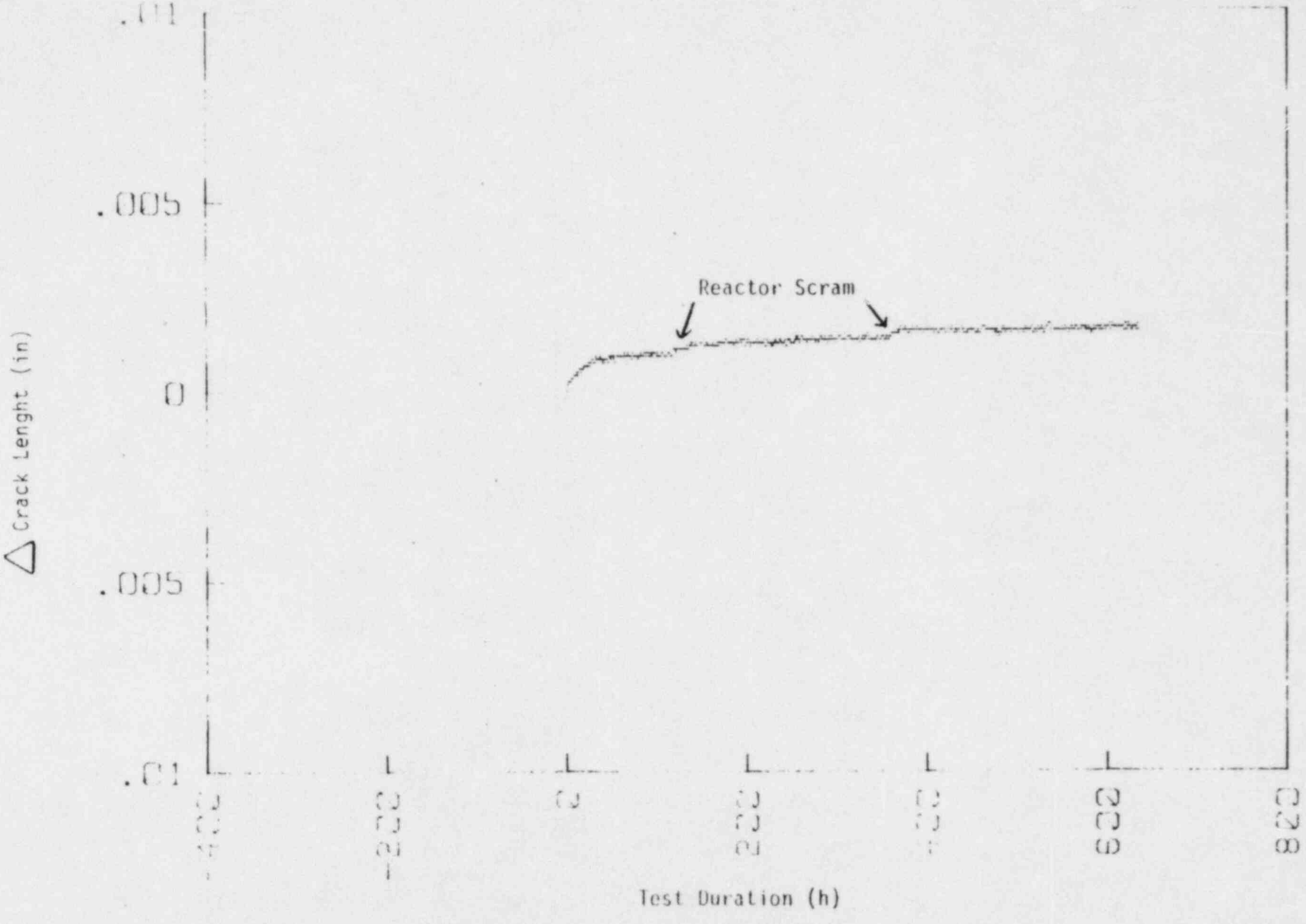


Figure 17. Dresden-2 HWC Crack Growth Test on Furnace Sensitized Type 304 Stainless Steel, K = 27.5 MPa/m



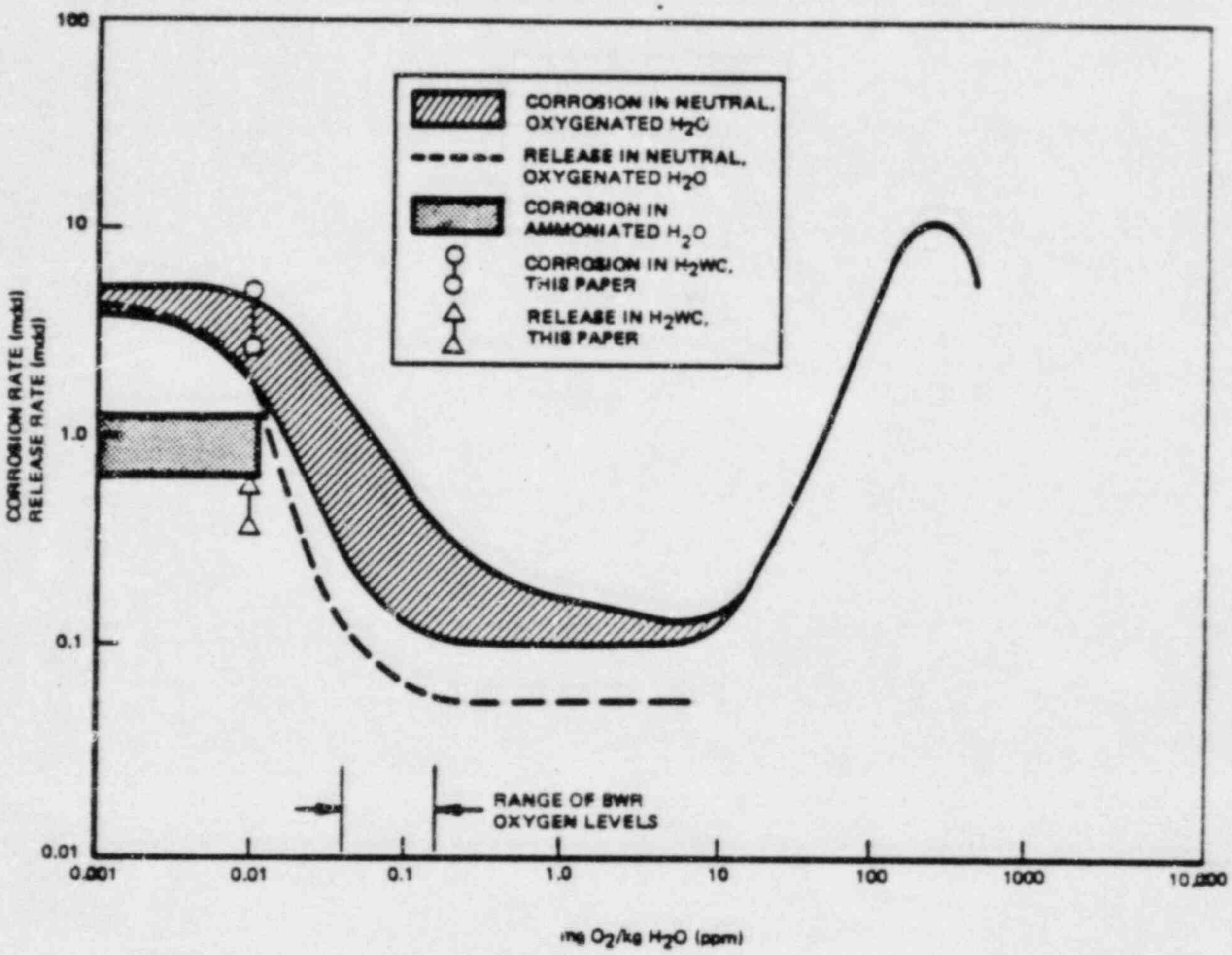


Figure 18. Corrosion Rates and Release Rates for Carbon Steel at Different Oxygen Concentrations for 1,000 h Exposure Times at Temperatures in the Range 200-300°C (392-572°F). (Compiled by Urbanic, V. F., from orginal corrosion data and numerous results published in the literature.

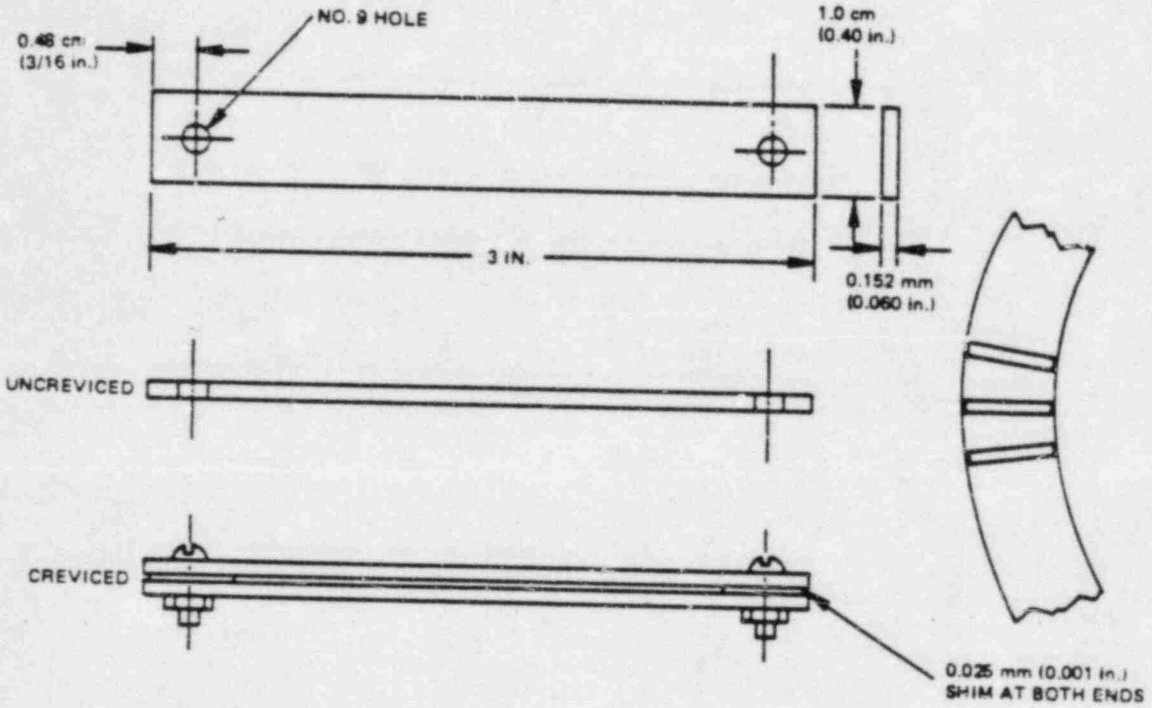
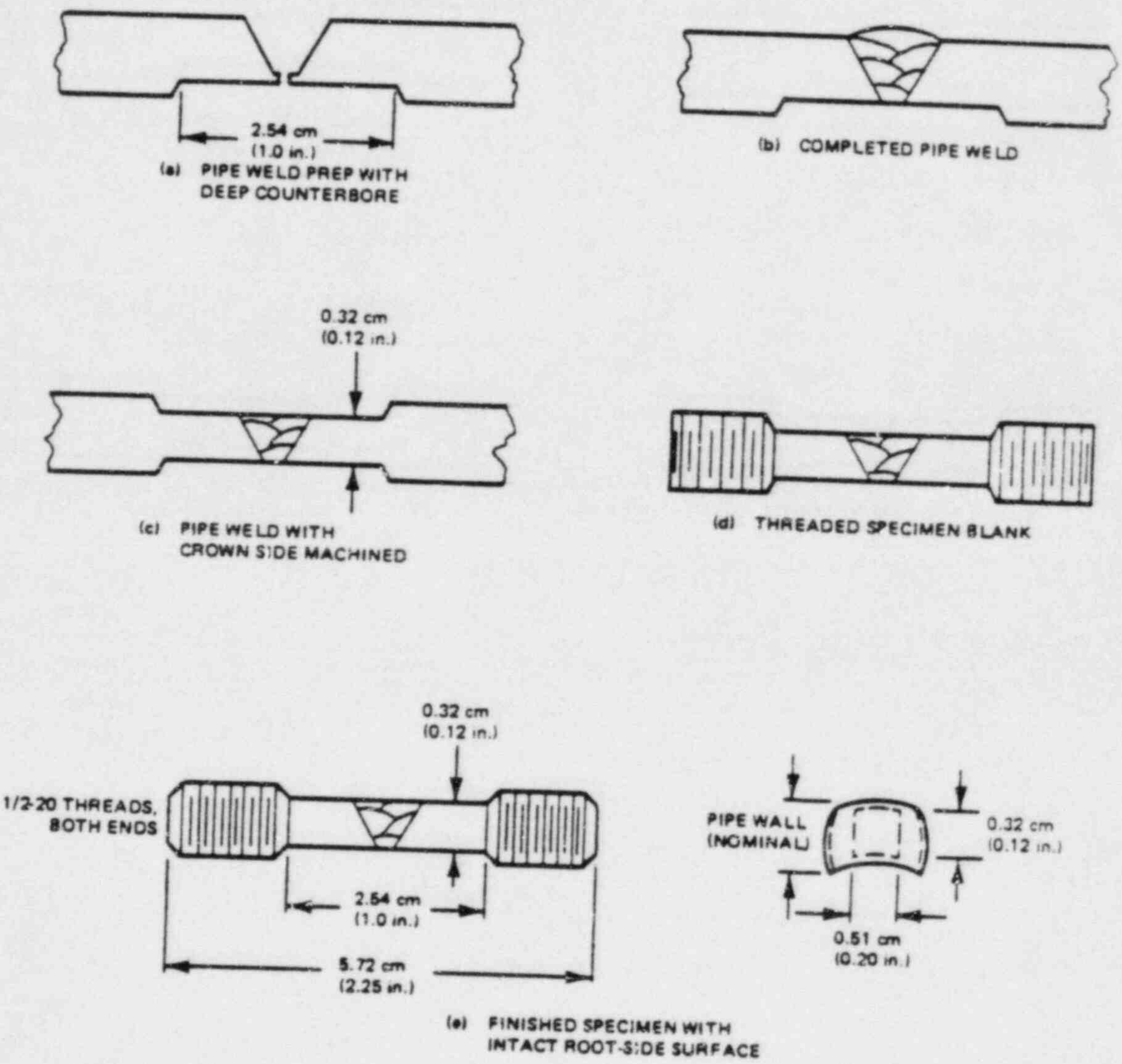


Figure 19. General, Crevice and Galvanic Corrosion Specimens



(a) PIPE WELD PREP WITH DEEP COUNTERBORE

(b) COMPLETED PIPE WELD

(c) PIPE WELD WITH CROWN SIDE MACHINED

(d) THREADED SPECIMEN BLANK

(e) FINISHED SPECIMEN WITH INTACT ROOT-SIDE SURFACE

Figure 20. Fabrication Sequence for Welded Constant Load Tensile Specimen

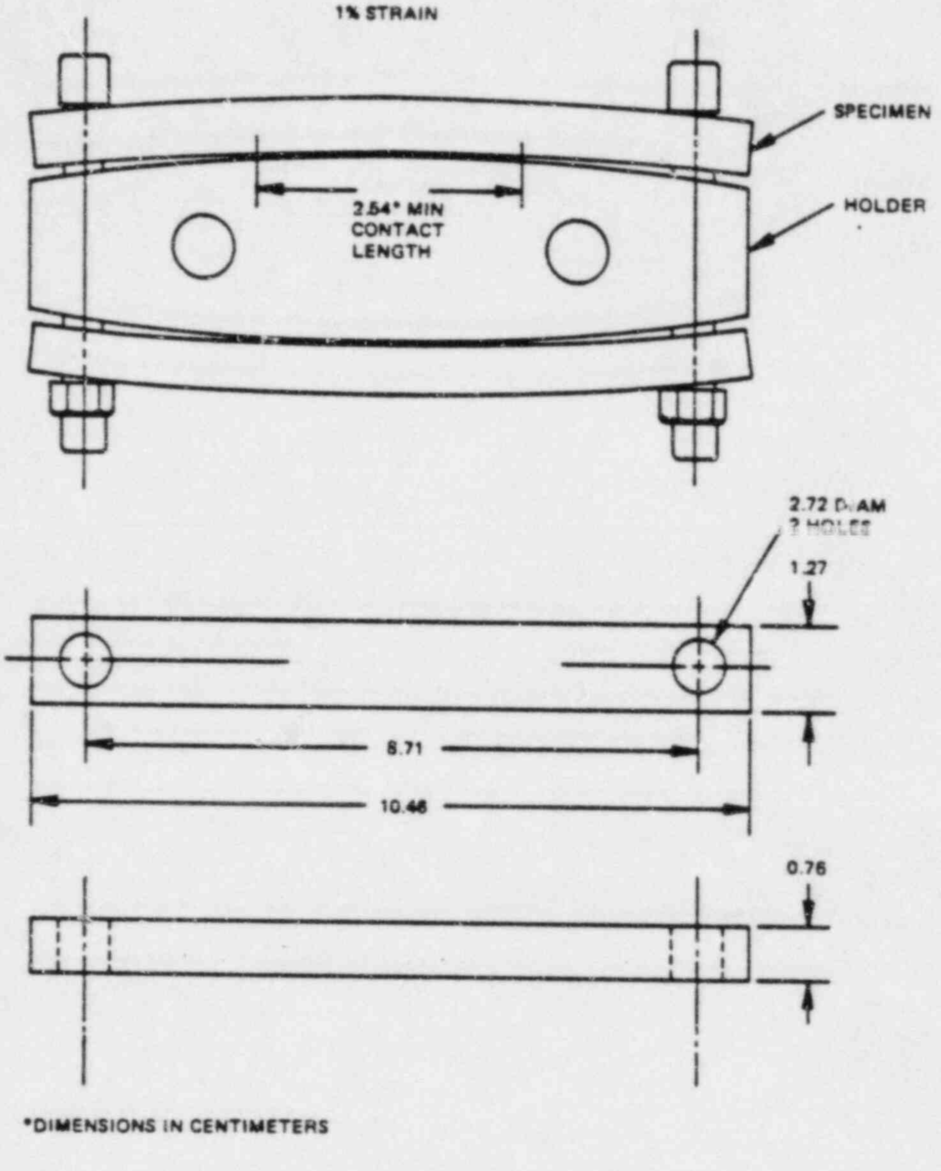


Figure 21. Bent Beam Specimen and Test Fixture

APPENDIX B.

ROLE OF IMPURITIES ON IGSCC AND HWC - ARGONNE NATIONAL LABORATORIES STUDIES

Extensive studies to assess the effectiveness of Hydrogen Water Chemistry in mitigating stress corrosion cracking of stainless steel have been conducted at Argonne National Laboratories.[1]

Three basic types of evaluations have been conducted. First, constant extension rate tests were conducted under controlled potential and conductivity to assess the critical potential and conductivity where IGSCC is eliminated as a function of conductivity. The studies were conducted on solution annealed Type 304 stainless steel, lightly sensitized Type 304 stainless steel, and heavily sensitized Type 304 stainless steel. The conductivity was adjusted by application of controlled amounts of NaH_2SO_4. The constant extension rate tests were were conducted in water at 288°C. The results of the studies are shown in Figure 1, a plot of corrosion potential vs. conductivity at 25°C. The corrosion potential was measured as part of each test. In general, the data show that as conductivity increases, the corrosion potential required to prevent IGSCC becomes more negative. Measurements of stainless steel corrosion potential at Dresden-2 have shown that under Hydrogen Water Chemistry conditions, values considerably less than -350 mV (SHE) can be expected for long term operation. These corrosion potential condition values result in IGSCC mitigation if the conductivity is 0.3 uS/cm or less with Na_2SO_4 as the impurity. These tests are quite relevant to reactor operations since this type impurity can enter the reactor recirculation system through leakage of resin beds. The data curve shown is for heavily sensitized Type 304 stainless steel but very similar results were found for lightly sensitized stainless steel.

In addition to the controlled potential CERTS described above, additional CERTs were conducted wherein coolant oxygen and conductivity were systematically varied. As in the potential controlled tests, conductivity was varied by Na^2SO^4 additions. Results were similar to those in the controlled potential tests in that when coolant oxygen was reduced to about 20 ppb, corresponding to a corrosion potential of -350 mV (SHE) , no IGSCC was obtained if conductivity did not exceed 0.3 uS/cm.

The second basic type of study involved an evaluation of a very broad range of coolant impurity species. At first, nine different types of impurities were evaluated as shown in Figure 2. Significantly, none of the impurities evaluated were more severe in promoting IGSCC than the Na_2SO_4 used to conduct the studies described above. These results were followed up by a study of sulfate with several different types of cations. Results, shown in Figure 3, indicate that although some cations are slightly more severe than Na_2SO_4, the main result still holds that no IGSCC is expected if the corrosion potential is below -350 mV (SHE) if conductivity does not exceed about 0.3 uS/cm.

The third basic area of study was a crack growth study on both sensitized and solution annealed Type 304 stainless steel. Both heavily and lightly sensitized material were evaluated. As shown in Figure 4, no crack growth was observed in the sensitized stainless steel when oxygen in the coolant was reduced from 200 ppb to 20 ppb oxygen. Crack growth rates were re-established at their original rates when the coolant oxygen was increased from 20 ppb to 200 ppb.

In summary, the results of these studies show for a broad range of coolant impurities, no IGSCC is expected if the corrosion potential is below -350 mV (SHE) and the conductivity does not exceed 0.3 uS/cm. These corrosion potentials are achieved in Dresden-2 when the coolant oxygen is less than 20 ppb. Moreover, the crack growth data show that pre-existing cracks can be stopped if coolant oxygen is reduced to 20 ppb.

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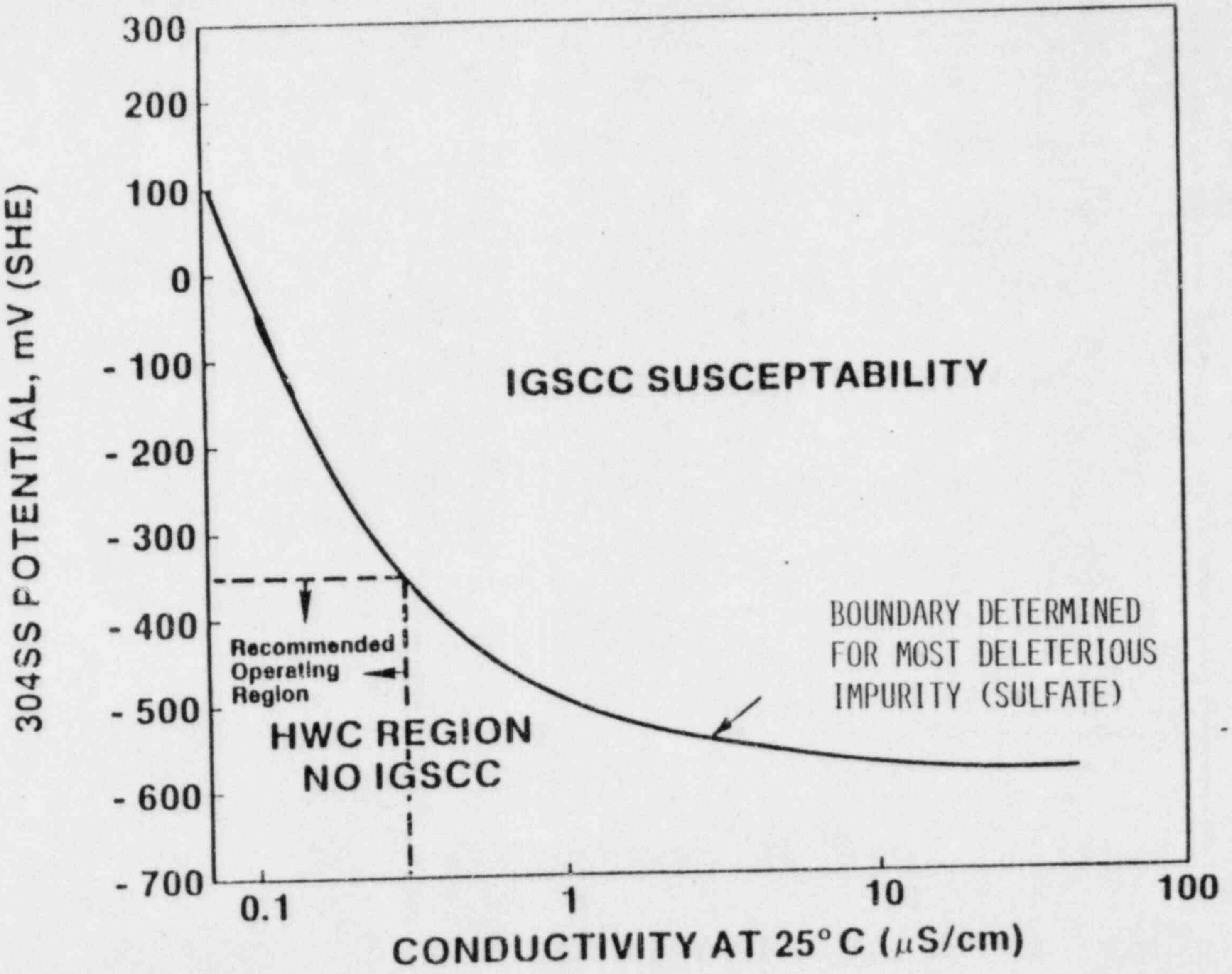
[1] T. Kassner, paper presented at General Electric, Argonne National Labs., NRC, EPRI Seminar on IGSCC Studies. San Jose, California, March, 1984.

FIGURE 1

CERT EXPERIMENTS ON SENSITIZED TYPE 304SS IN SIMULATED BWR - QUALITY WATER AT 289° C

(DATA FROM ARGONNE NATIONAL LABORATORY)



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ARGONNE NATIONAL LABS STUDY

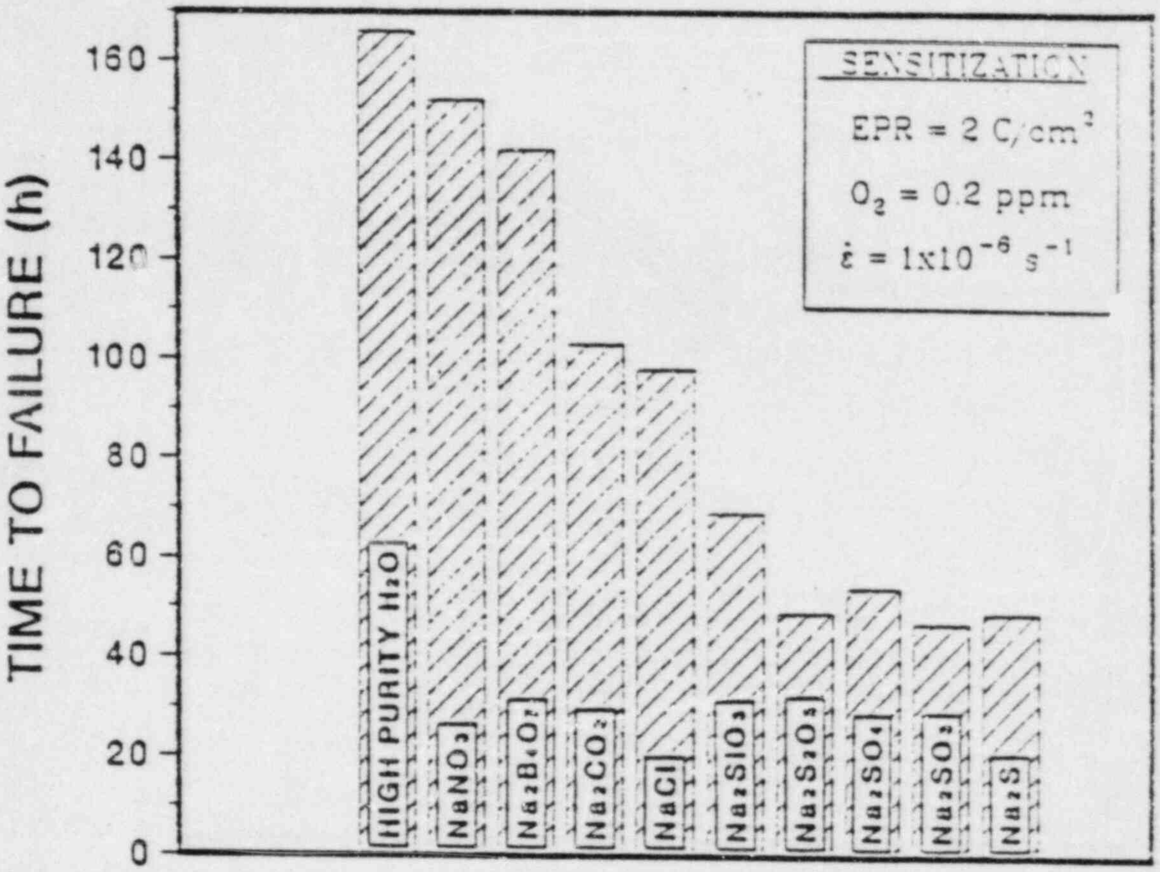


Fig. 2 Effect of Various Anion Species at a Concentration of 0.1 ppm With Sodium in 289°C Water Containing 0.2 ppm Dissolved Oxygen on the Time to Failure of Lightly Sensitized (EPR = 2 C/cm^2) Type 304 SS Specimens in CERT Experiments at a Strain Rate of 1×10^{-6} s^{-1}.

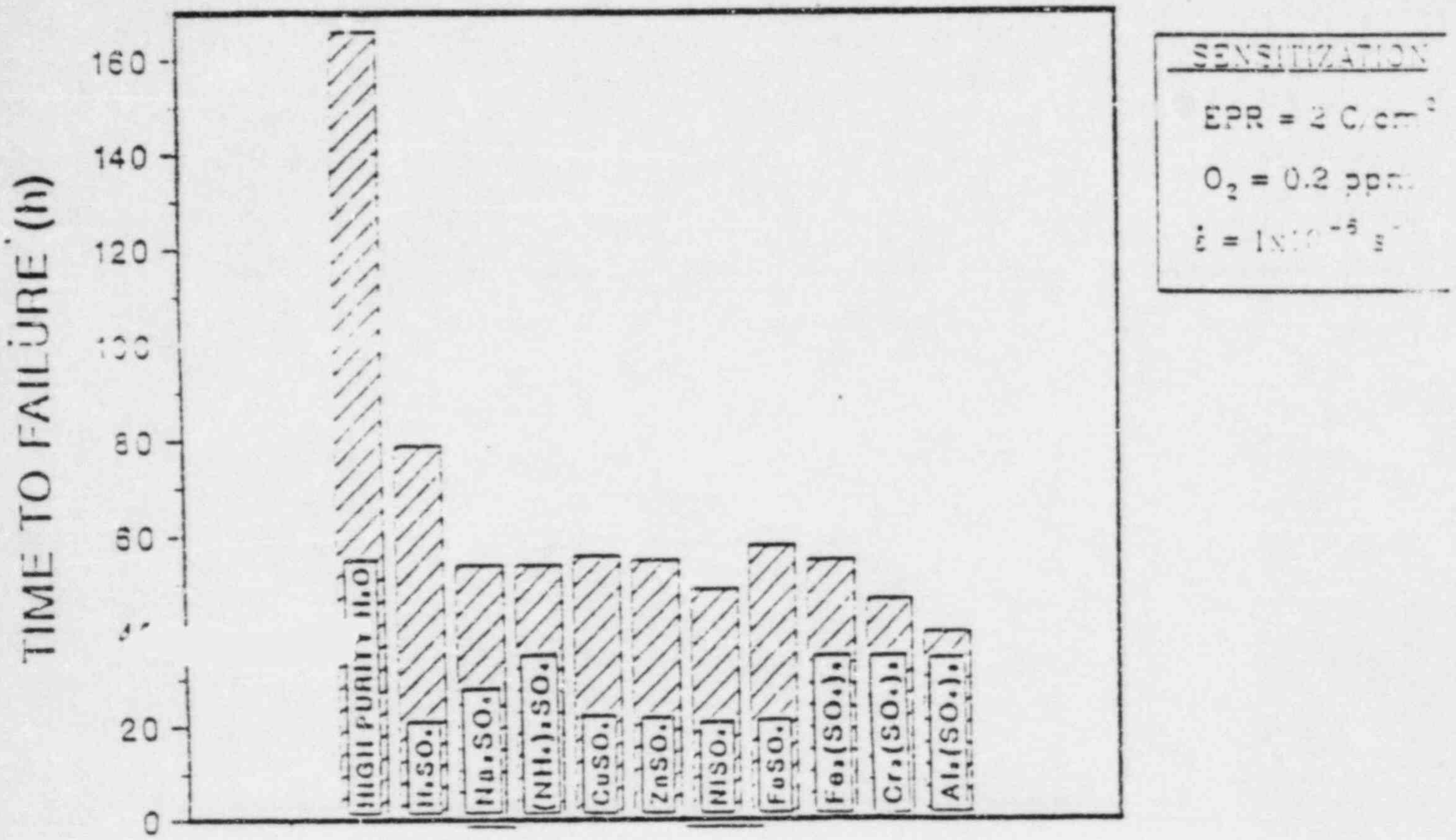
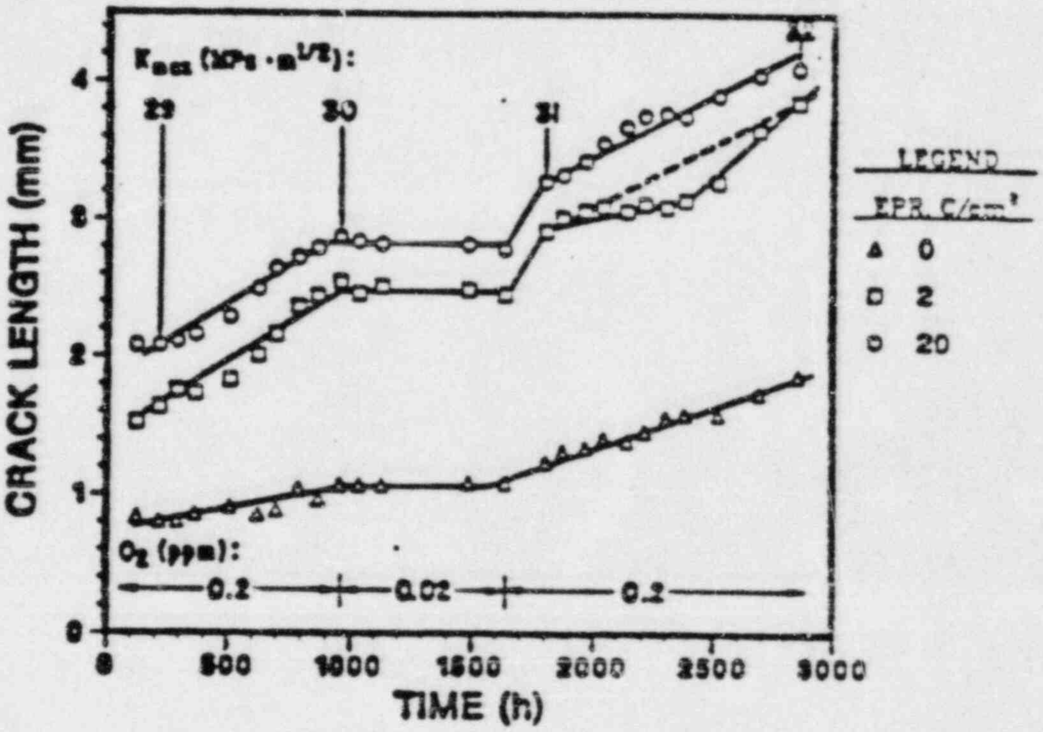


Fig. 3 Effect of 0.1 ppm Sulfate with Different Cations on the Time to Failure of Lightly Sensitized (EPR = 2 C/cm^2) Type 304 SS Specimens in CERT Experiments at a Strain Rate of $1 \times 10^{-6}\ s^{-1}$ in 289°C Water with 0.2 ppm Dissolved Oxygen.

FIGURE 4

ARGONNE NATIONAL LABORATORY DATA:



HWC Arrests Crack Growth In Sensitized
T-304 SS Under Slow Cyclic Loading

APPENDIX 3.

ION CHROMOTAGRAPHY MEASUREMENT PROGRAM

Introduction

Ion chromatography has proven to be a valuable research tool in many industrial applications. It has the advantages of both qualitative and quantitative analyses for a variety of ionic species. Moreover, the technique affords very good sensitivities for most chemical species: frequently, concentrations of less than 0.1 ppb can be accurately measured with a high degree of confidence. Samples can also be completely characterized in a reasonable time frame, with determination rates on the order of several samples per hour. Because of the many advantages afforded by this technique, ion chromatography is rapidly finding diverse applications in many BWR chemistry laboratories. Many BWR chemistry groups now routinely use the ion chromatograph for daily reactor water chloride measurements, and have abandoned the more cumbersome techniques of colorimetry, turbidimetry, and electrochemistry. Others have used ion chromatography for assessing the performance of the condensate treatment and reactor water cleanup systems for a variety of chemical species. Condenser leak rates may also be assessed by low-level sodium and chloride measurements.

ION CHROMATOGRAPHY MEASUREMENT PROGRAM

During a one-month demonstration test conducted in 1982, and for the entirety of Fuel Cycle 9 (April, 1983 to present), the Dresden-2 reactor has operated on hydrogen water chemistry. In a very repeatable fashion, both the reactor water conductivity and the reactor water pH increase when the hydrogen addition system is turned on: conversely, when the hydrogen addition system is shut down, both parameters decrease. Calculations have shown that the changes in conductivity can be attributed to the changes in pH, regardless of the status of the hydrogen addition system, i.e. on or off. These changes are thought to be the result of a change in the concentration of the equilibrium radiolysis products when the core changes from an oxidizing to a more reducing environment when the hydrogen addition system is turned on, or, the reverse when the hydrogen addition system is shut down.

The dramatic change in the core oxidizing potential as a result of hydrogen addition may produce some chemical changes that would not be detected by ordinary chemical monitoring instrumentation. Possible reactions that might occur with the implementation of hydrogen water chemistry would be the conversion of ferric to ferrous iron, the reduction of nitrate ion to nitrite and/or ammonium ions, or to gaseous nitrogen oxides, or the reduction of hexavalent chromium to insoluble chromium trioxide. The documentation of these reactions (or their absence) would further assist in the complete understanding of the implications of hydrogen water chemistry. Accordingly, the Electric Power Research Institute contracted with the General Electric Company to perform ion chromatography measurements at the Dresden-2 reactor. The first measurement campaign was performed in February and March of this year. The results summarizing this campaign are the basis of this report. A second series of measurements is planned for the first quarter of 1985. These data will be compared to the 1984 campaign to see if any changes will have occurred as the result of an additional year of operation with hydrogen water chemistry.

Equipment and Installation

The mainframe instrument used for this series of measurements was a Dionex Model 2020i Liquid Ion Chromatograph Three operating channels were used in this configuration: monovalent cations, anions, and transition metal ions. Detectors for the anion and cation channels were Dionex Conductivity Detectors, while the transition metal ion detector was a Dionex Opti-Ion UV/Visible single-beam spectrophotometer. For all three channels, eluents were pumped through the columns and detectors using Dionex high-pressure Analytical Pumps. Anion and cation regenerant chemicals were introduced to the system by gravity feed. The PAR reagent used in the detection of transition metals was housed in a one-liter glass bottle, and introduced to the system using pressurized argon. Columns used in the cation channel were HPIC-CS1 separator, HPIC-CG1 guard and concentrator, and CFS suppressor, all from Dionex. Columns for the anion channel included HPIC-AS4 separator, HPIC-AG4 guard and concentrator, and AFS suppressor. The fiber suppressor systems are extremely convenient, as they are configured for continuous regeneration. For the transition metal channel, a HPIC-CS2 separator and HPIC-CG2 guard and concentrator columns were used in conjunction with a postcolumn membrane reactor.

Customized automatic sample changing modules were built for this test. For the cation and anion channels, an Eldex Model #AA100S dual-piston high pressure pump delivered sample water to the concentrator columns: for the transition metal channel, the concentrator column was loaded by an Eldex Model #B100S single piston high-pressure pump. Automatic sample changing was controlled by air-actuated 10-port rotary valves. Minarek programmers were used to sequence the operation of the sample changer and the ion chromatograph. The basic steps of the program consisted of a three-minute line flush, a 10-to-15 minute period for loading the sample onto the concentrator columns, a 15 minute period for column elution and generation of the chromatogram, and sample changing. The program was written to accomodate 10 sample changes, and then shut the sytem down automatically, thus allowing unattended operation. Anion and cation chromatograph outputs were monitored on a Linear Model 585 strip chart recorder, while the transition metal chromatographs were maintained on a Hewlett-Packard Model 3885 integrating strip chart recorder.

Reagents and Standards

All chemicals used in this study were reagent grade quality or better. Eluent and regenerant solutions were prepared in 8-liter quantities, and were stored in polypropylene Nalgene Lowbouys. The eluent solutions were 0.008M HCl for the cations, 0.003M Na_2CO_3/0.003M $NaHCO_3$ for the anions, while the transition metal eluent contained 1.26 g/l oxalic acid, 1.57 g/l citric acid, and 1.22 g/l LiOH. The regenerant solutions were 0.025M H_2SO_4 for the anions, and 0.02M tetramethylammonium hydroxide for the cations. The photochromic solution for the transition metal ion detector contained 207 ml 30% ammonium hydroxide, 57 ml glacial acetic acid, and 0.1 g 4-(2-Pyridylazo)resorcinol monosodium salt, monohydrate per liter of solution, hereafter referred to as PAR.

Mixed cation standards were prepared from NaCl, NH_4Cl, and K_2CO_3. The stock solution contained 1000 ppm of each cation, and was prepared and stored in a plastic volumetric flask. Mixed anion standards were prepared from NaCl, $NaNO_2$, $NaNO_3$, K_2SO_4, K_2HPO_4, and $Na_2C_2O_4$, again in 1000 ppm concentrations for each anion, and stored in a plastic flask. Individual transition metal standards for Fe, Cu, Ni, and Zn in 1000 ppm concentrations were obtained from Spex Industries. Instrumental working standard concentrations were 5 and 10 ppb of each species, and were prepared by appropriate dilutions of the stocks in plastic volumetric flasks. These working solutions were prepared daily. The water used in the dilution of the primary standard also served as the daily blank. Some problems were encountered finding good-quality water for the preparation of standards and blanks. The concentrations of sodium and chloride impurities in the laboratory demineralized water supply were very dynamic, and often contained salt concentrations in excess of 10 ppb. Generally, the most suitable water in the plant for the preparation of standards and blanks was the effluent of the condensate treatment system

Sample Points

Seven sample points were monitored on a daily basis. The list of acronyms associated with these points is as follows:

(1) CDI--Condensate Demineralizer Inlet
(2) CDE--Condensate Demineralizer Effluent
(3) FFW--Final Feedwater
(4) RCI--Reactor Water Cleanup System Inlet
(5) RCEA--"A" Reactor Water Cleanup Demineralizer Effluent
(6) RCEB--"B" Reactor Water Cleanup Demineralizer Effluent
(7) MST--Main Steam

CDI, CDE, and FFW samples were obtained from grab sample taps in the turbine building sample sink. RCI, RCEA, and RCEB samples were obtained from the reactor building sample sink. MST samples were obtained from a grab sample tap off the General Electric process instrument line located immediately outside the X-Area wall. Several precautionary measures were taken to obtain representative, uncontaminated samples. Sample containers were 250 ml plastic culture bottles. These bottles were filled with water from the respective sample points, and were soaked in for a three day period prior to use. Sample bottles and their caps were labelled and dedicated to their respective streams. The CDI and CDE sample taps were manifolded to a common effluent at the turbine building sample sink, as were the RCI, RCEA, and RCEB sample taps in the reactor building sample sink. Prior to obtaining samples, each line was flushed for 10 minutes at a flow rate of roughly 1 liter per minute. Each bottle was filled, capped, shaken, and sample discarded four times before the actual sample was collected. Duplicate samples were obtained at each location--one for transition metals, the other for the cation/anion system.

Analyses

Roughly two hours were required for the acquisition of duplicate samples. Once obtained, they were transported to the ion chromatograph which was set up near the Unit-2 air compressors. Samples were segregated between transition metal and cation/anion botttles, and were positioned at the appropriate rotary valve ports. All lines between the grab sample bottles and the rotary valves were 0.125 in o.d. X 0.028 in wall teflon tubing. The following instrumental parameters were used for the three channels in the ion chromatography determinations:

	Cation	Anion	Trans. Metals
Eluent Flow (ml/min)	2.4	2.4	1.2
Sample Pressure (psig)	410	920	510
Lo Pres. Alarm (psig)	300	500	300
Hi Pres. Alarm (psig)	900	1200	1300
Sample Flow (ml/min)	2.90	3.19	3.16
Sample Volume (ml)	29.0	31.9	47.4
Detector Sensivity	3 uS/cm	3 uS/cm	0.2 A
Baseline Response	3.5 uS/cm	18.0 uS/cm	-----
Detector Temp. Comp.	1.7	1.7	-----

Blanks and standards were analyzed in an identical fashion to the samples. The net signal for each ion, standard minus blank, was used to calculate the concentrations. Blank readings were not subtracted from the sample readings. Owing to the dynamic impurity concentrations in the water used to prepare standards and blanks, it was not possible to determine the contribution of the analysis system to the samples.

Results and Discussion

Reactor power has always shown a pronounced effect on vessel chemistry at the Dresden-2 reactor. In general, the lower the power, the lower the vessel conductivity. Lower power results in lower impurity input per unit time, by allowing more efficient removal of impurities by the condensate treatment system (lower gpm/sq. ft), assuming the reactor water cleanup system flow rate remains constant. Figure 1 shows the reactor power and the reactor water conductivity (as read from a General Electric process instrument) during the ion chromatography measurement period. The symbols on the curves correspond to the actual data points when samples were collected and analyzed. The correlation between the two parameters is apparent. Full power at the Dresden-2 reactor is roughly 2527 MWt, and the plant operated at neraly full power for the last week of the testing period. The maximum vessel conductivity that was observed was 0.14 uS/cm. Contributing to the achievement of low vessel conductivity is the design basis of the reactor water cleanup system which was operating at 6.6% of rated feedwater flow (about 1200 gpm). From a conductivity standpoint, the Dresden-2 reactor currently has one of the best vessel chemistries of all domestic BWR's.

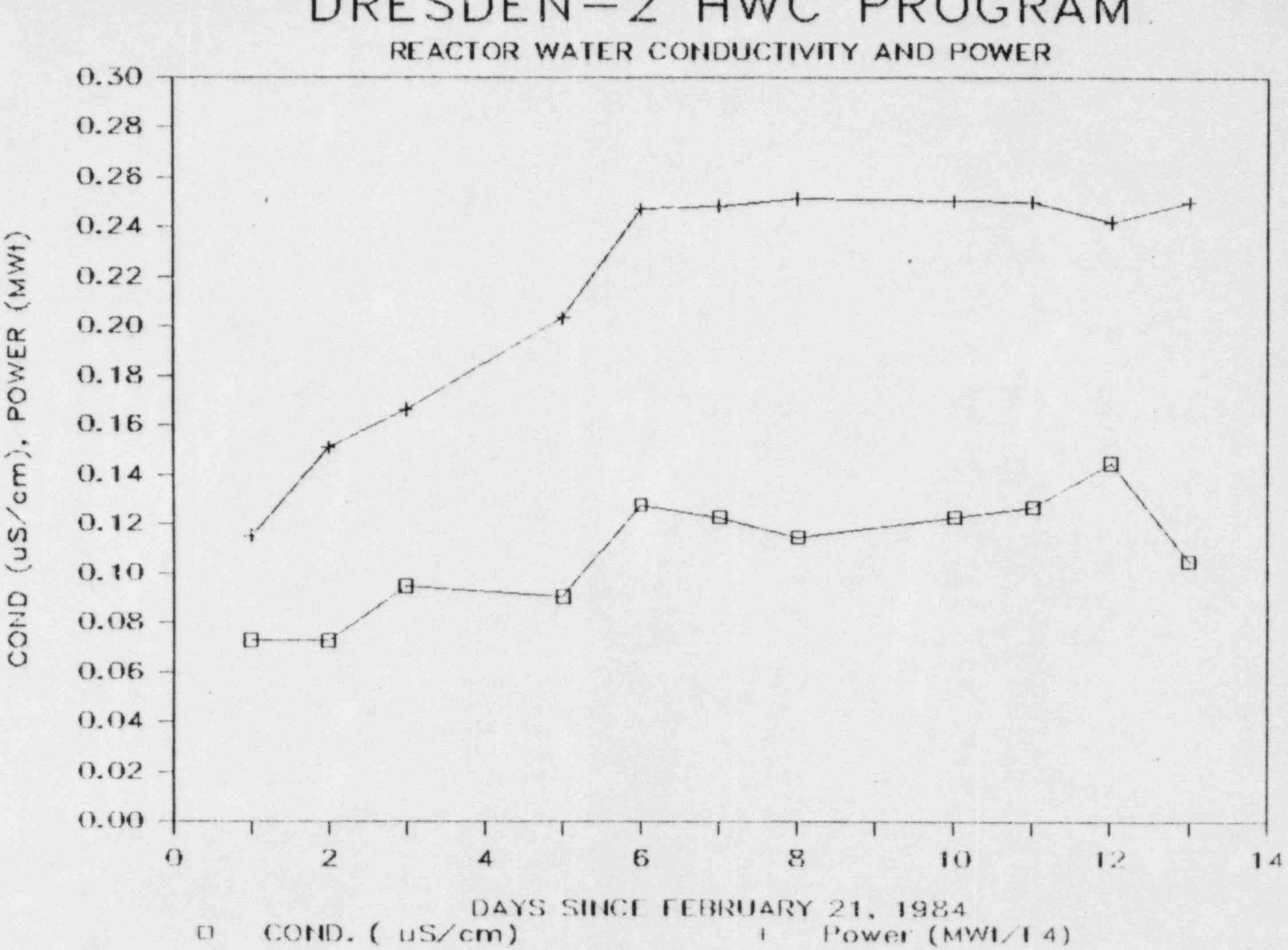
The dissolved gas concentrations in the reactor water, main steam, and final feedwater are shown in Figures 2 through 5, respectively. The data point symbols correspond to the time periods when samples were collected. The hydrogen addition system was shut off on four separate days during the testing interval, as indicated by concentrations of less than 20 ppb dissolved oxygen in the primary coolant (Figure 2), and feedwater dissolved hydrogen concentrations less than 40 ppb (Figure 5). Subtle differences in the concentration of ionic impurities as a result of hydrogen addition status may not be readily apparent during such a short testing interval. The dissolved oxygen concentration in the feedwater ranged between 15 and 59 ppb during the measurement campaign, generally within the Fuel Warranty Operating Limit range of 20-200 ppb.

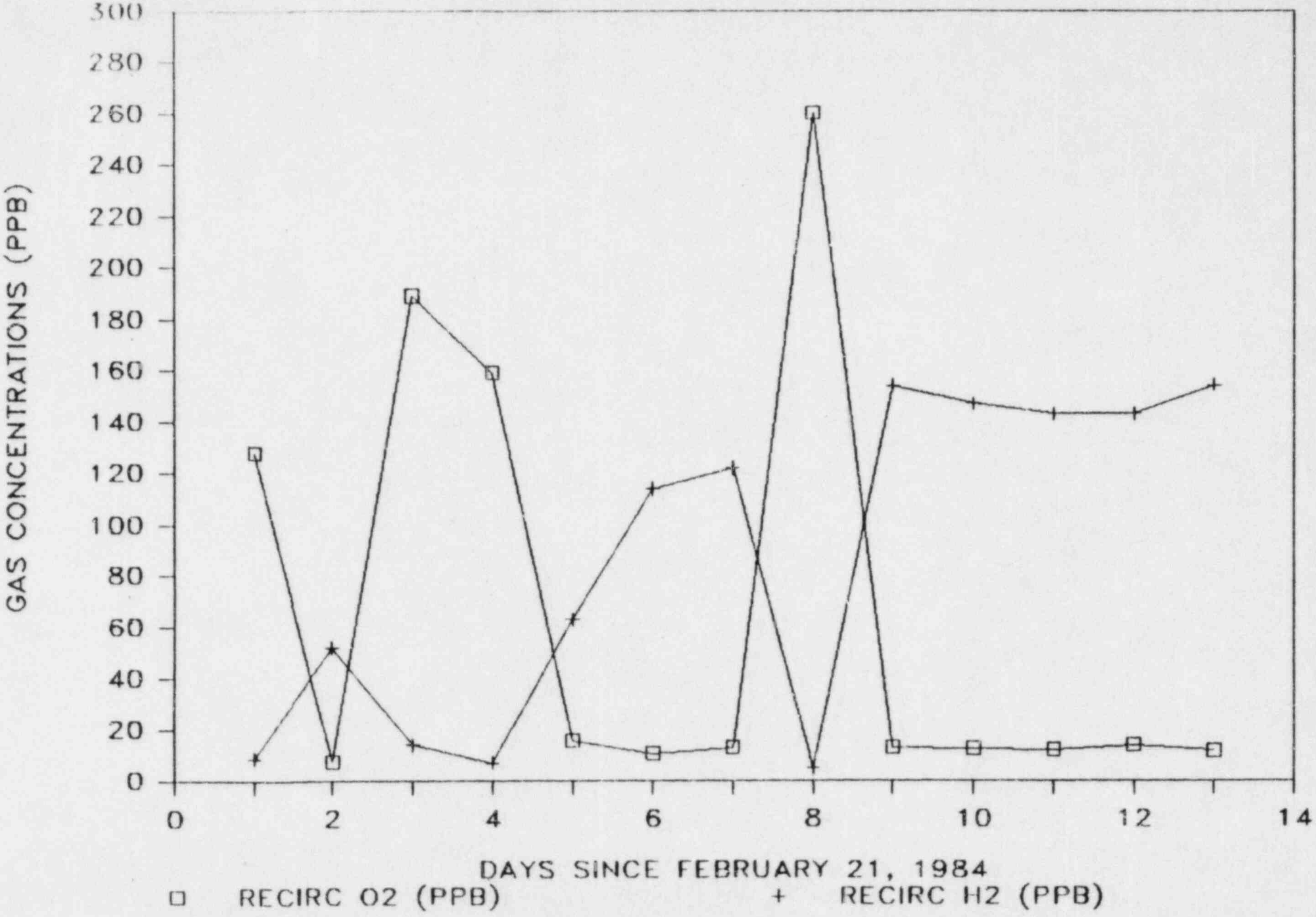
Condensate-Feedwater Results

Tables 1 through 3 show the ion chromatography measurements for the CDI, CDE, and FFW samples, respectively.

Several ions that constituted the makeup of the standard solutions are conspicuously absent from the table. The transition metal analyzer can simultaneously detect both ferrous and ferric iron along with copper, nickel and zinc. The sensitivity for both iron species is nearly tenfold less than the sensitivities for the remaining elements, and the sample sizes used for these analyses were probably not sufficient to allow good characterization using a full scale absorbance value of 0.2A. Although the 5 ppb ferric iron standard always generated a strong analytical signal, there were some problems in the resolution of this peak with the copper peak (partially resolved doublets). Real samples never showed doublets in this region of the chromatogram, and the sample retention times of the singlet peaks were

FIGURE 1

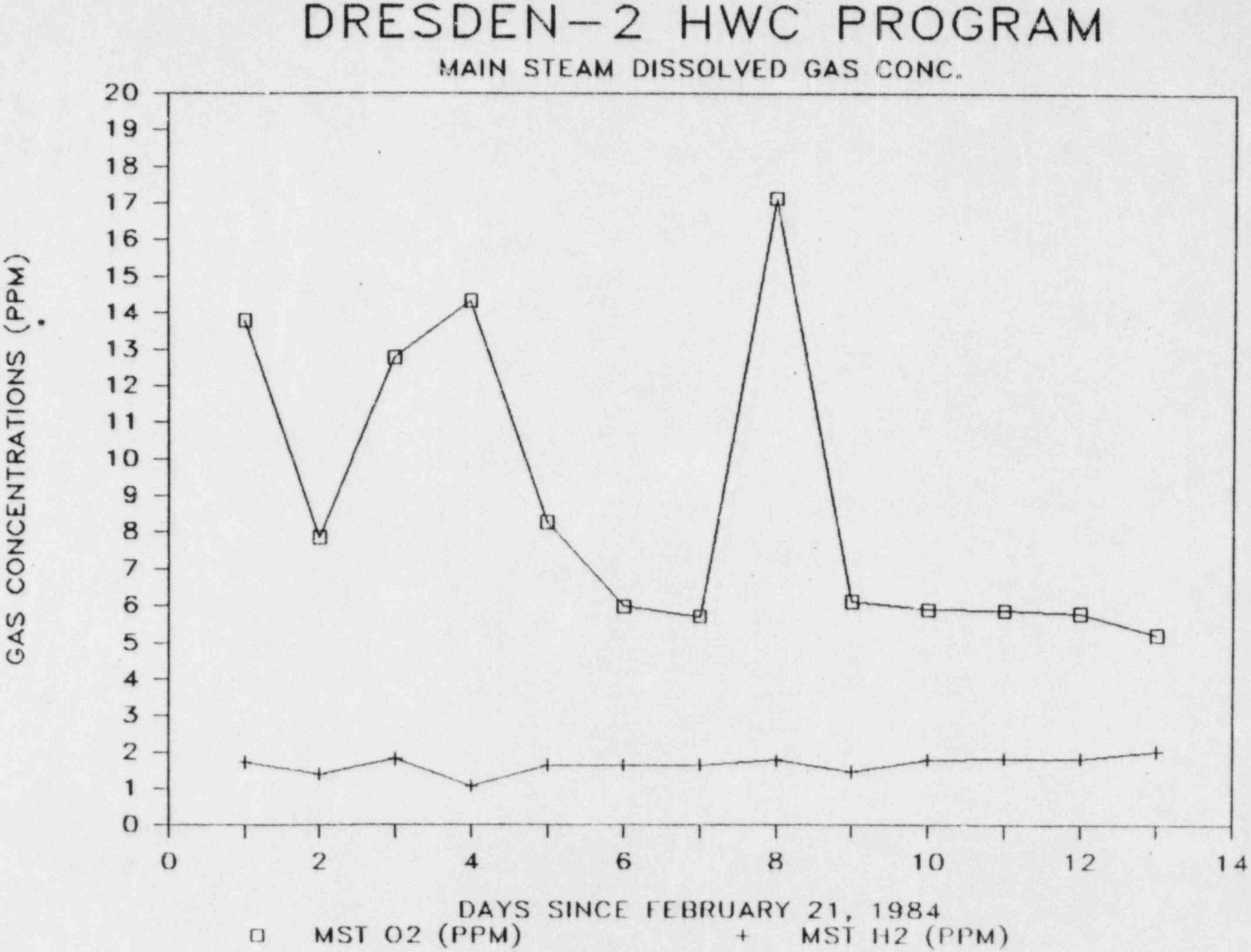

DRESDEN-2 HWC PROGRAM
REACTOR WATER CONDUCTIVITY AND POWER
COND (uS/cm), POWER (MWt)
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
2
4
6
8
10
12
14
DAYS SINCE FEBRUARY 21, 1984
□ COND. (uS/cm)
+ Power (MWt/14)



DRESDEN-2 HWC PROGRAM

RECIRC WATER DISSOLVED GAS CONC.

FIGURE 3


DRESDEN-2 HWC PROGRAM
MAIN STEAM DISSOLVED GAS CONC.
GAS CONCENTRATIONS (PPM)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
0
2
4
6
8
10
12
14
DAYS SINCE FEBRUARY 21, 1984
□ MST O2 (PPM)
+ MST H2 (PPM)

DRESDEN-2 HWC PROGRAM

FEEDWATER DISSOLVED OXYGEN CONC.

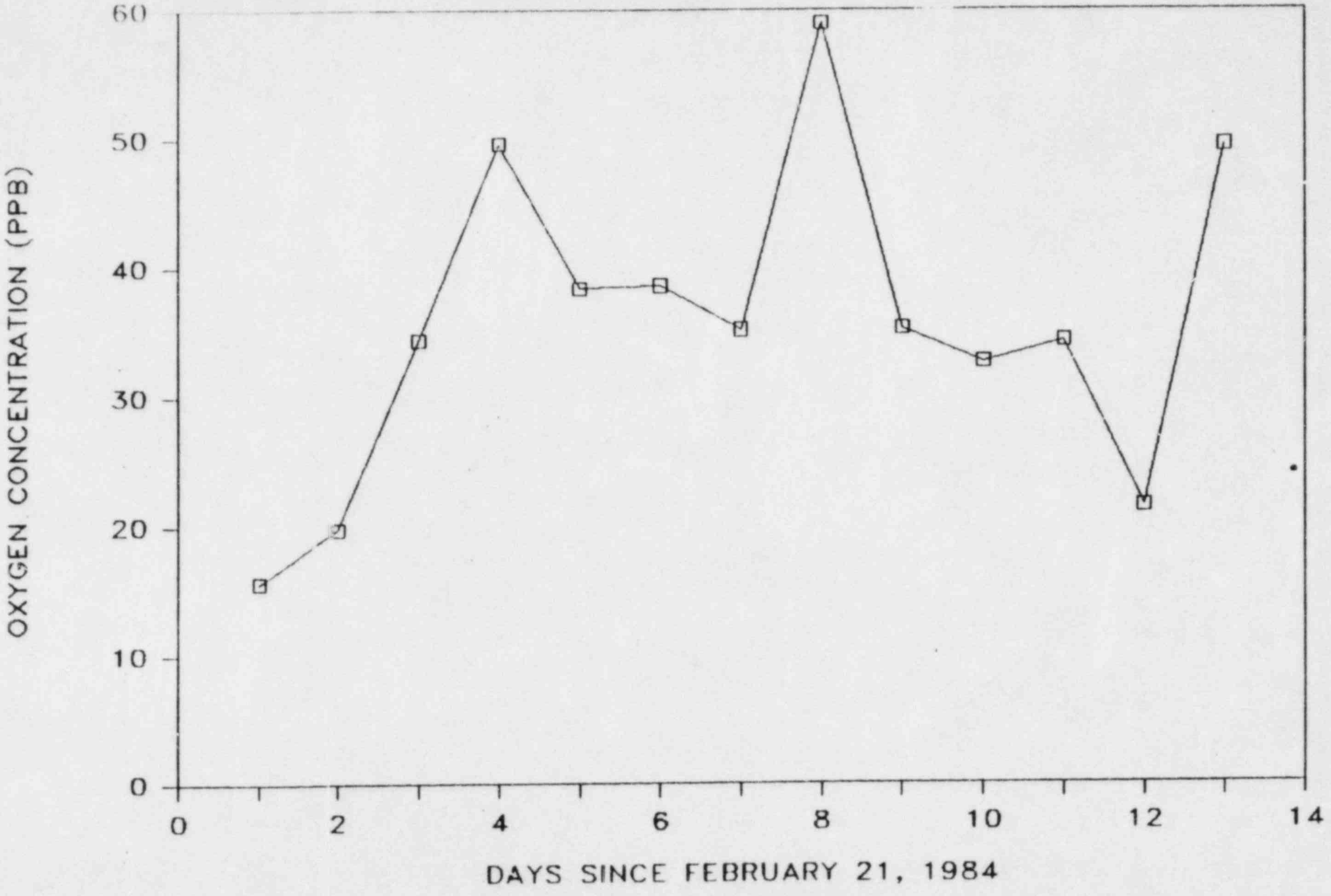
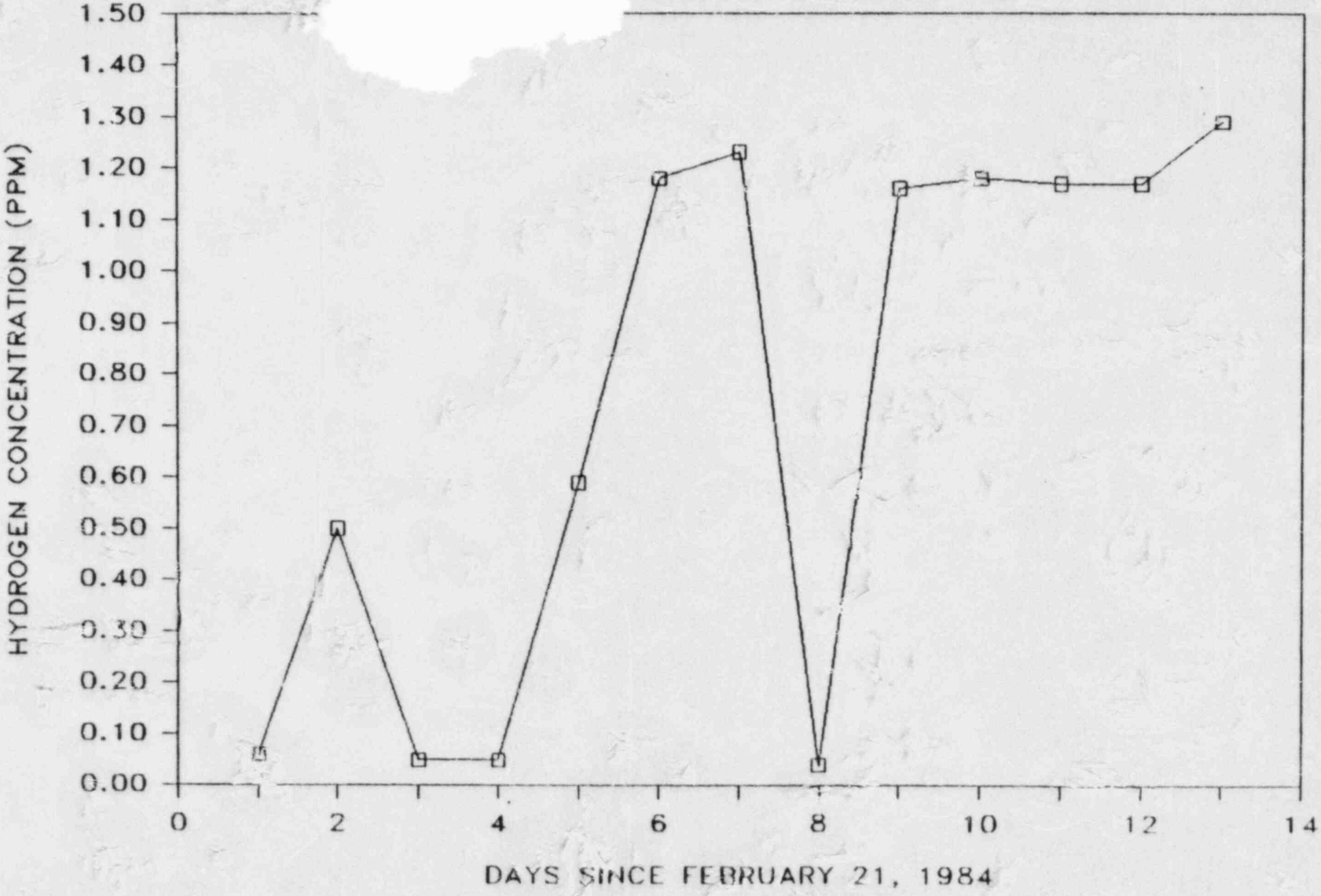


FIGURE 5

DR[illegible] HWC PROGRAM

[illegible]SSOLVED HYDROGEN CONC.



DRESDEN–2 HWC PROGRAM

COND. DEMIN. SODIUM PERFORMANCE

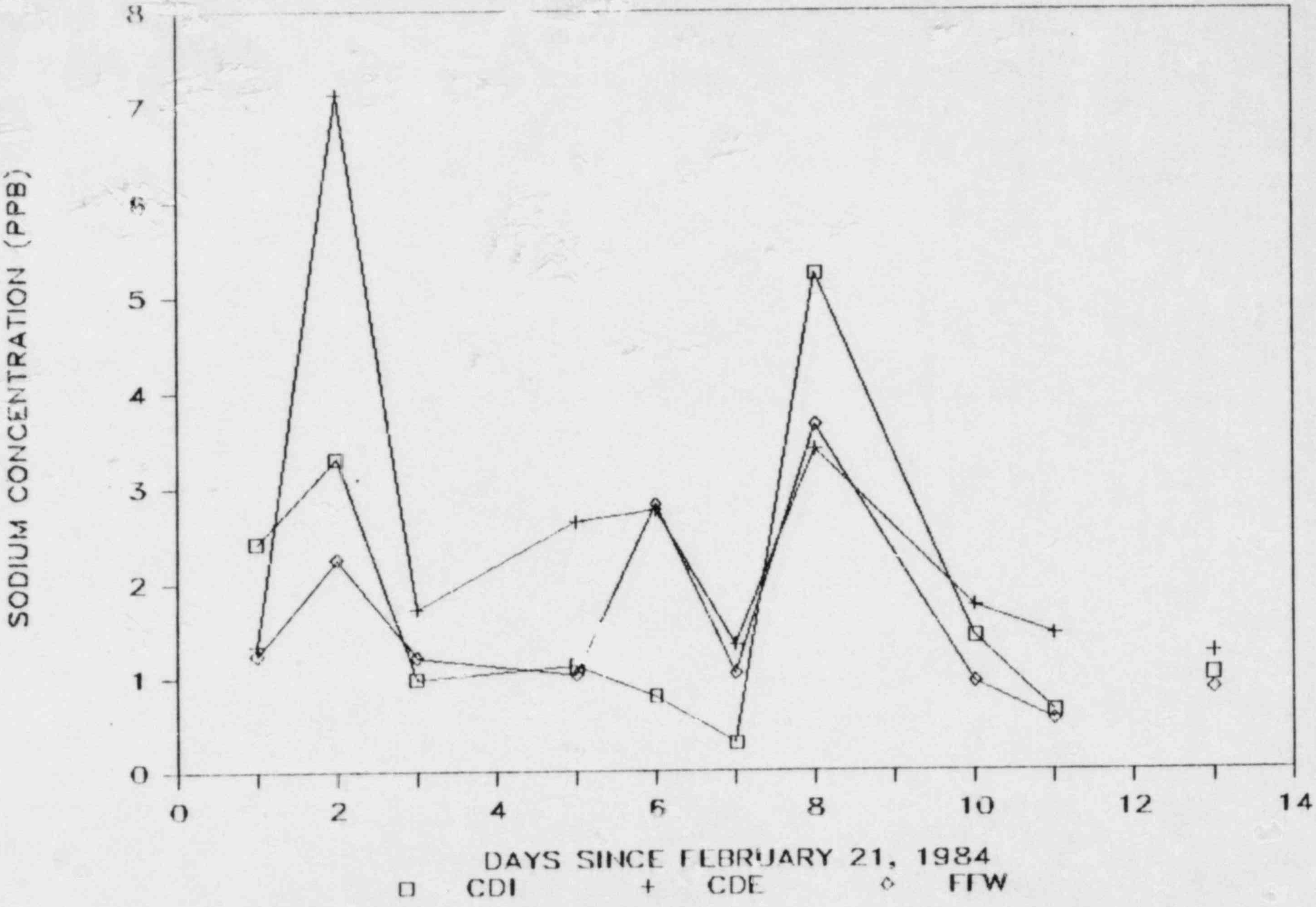
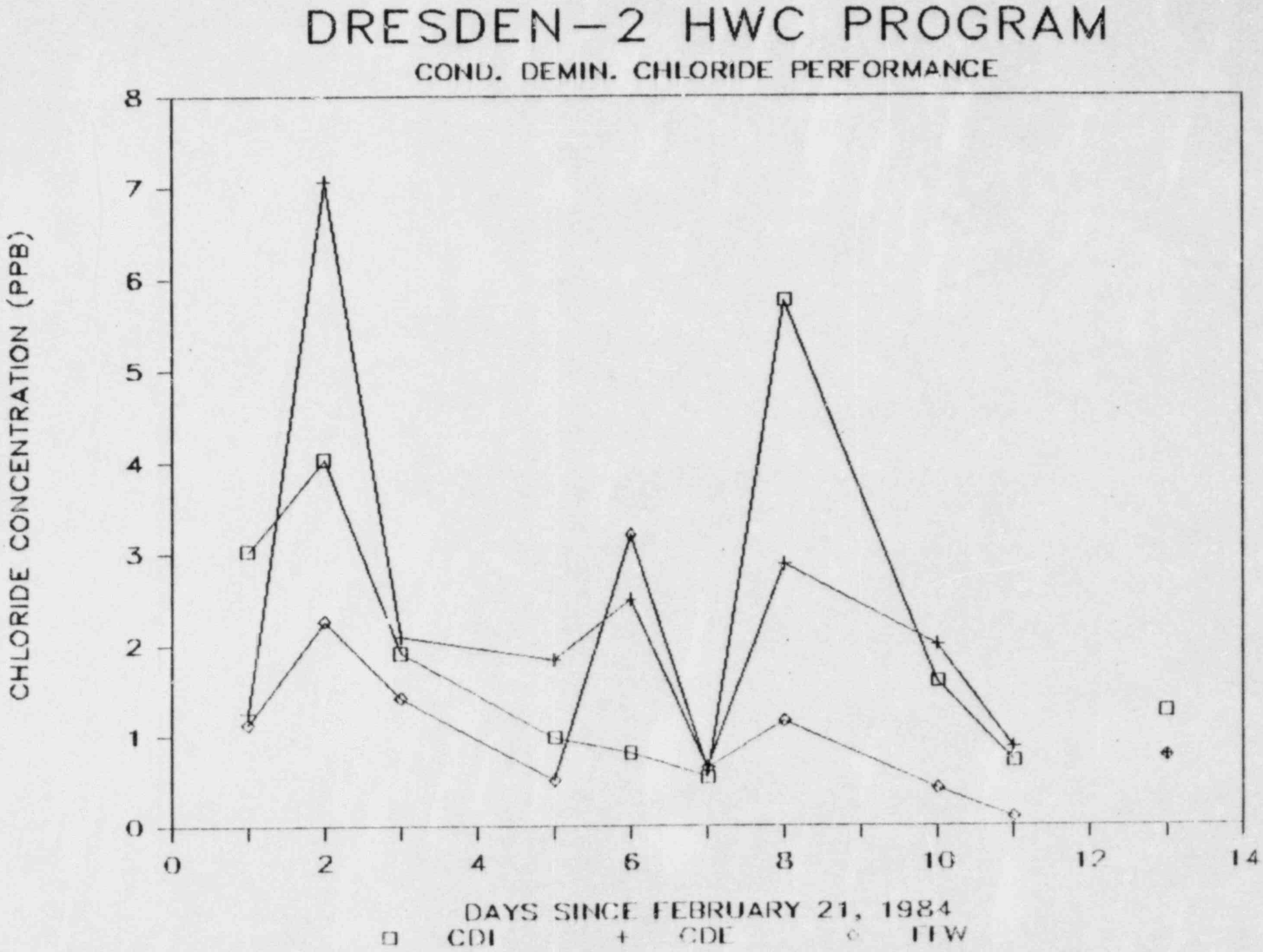
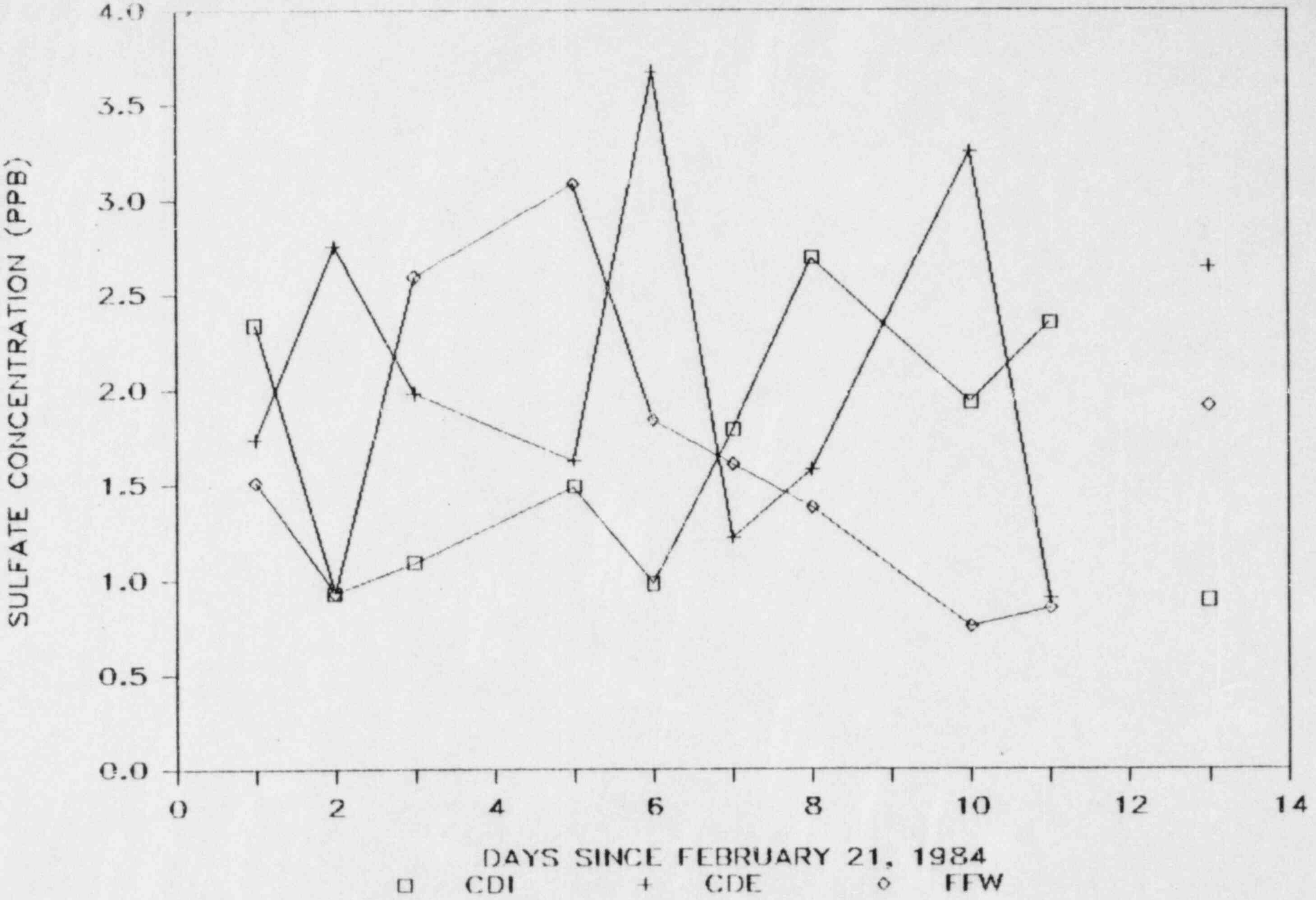


FIGURE 7



DRESDEN-2 HWC PROGRAM

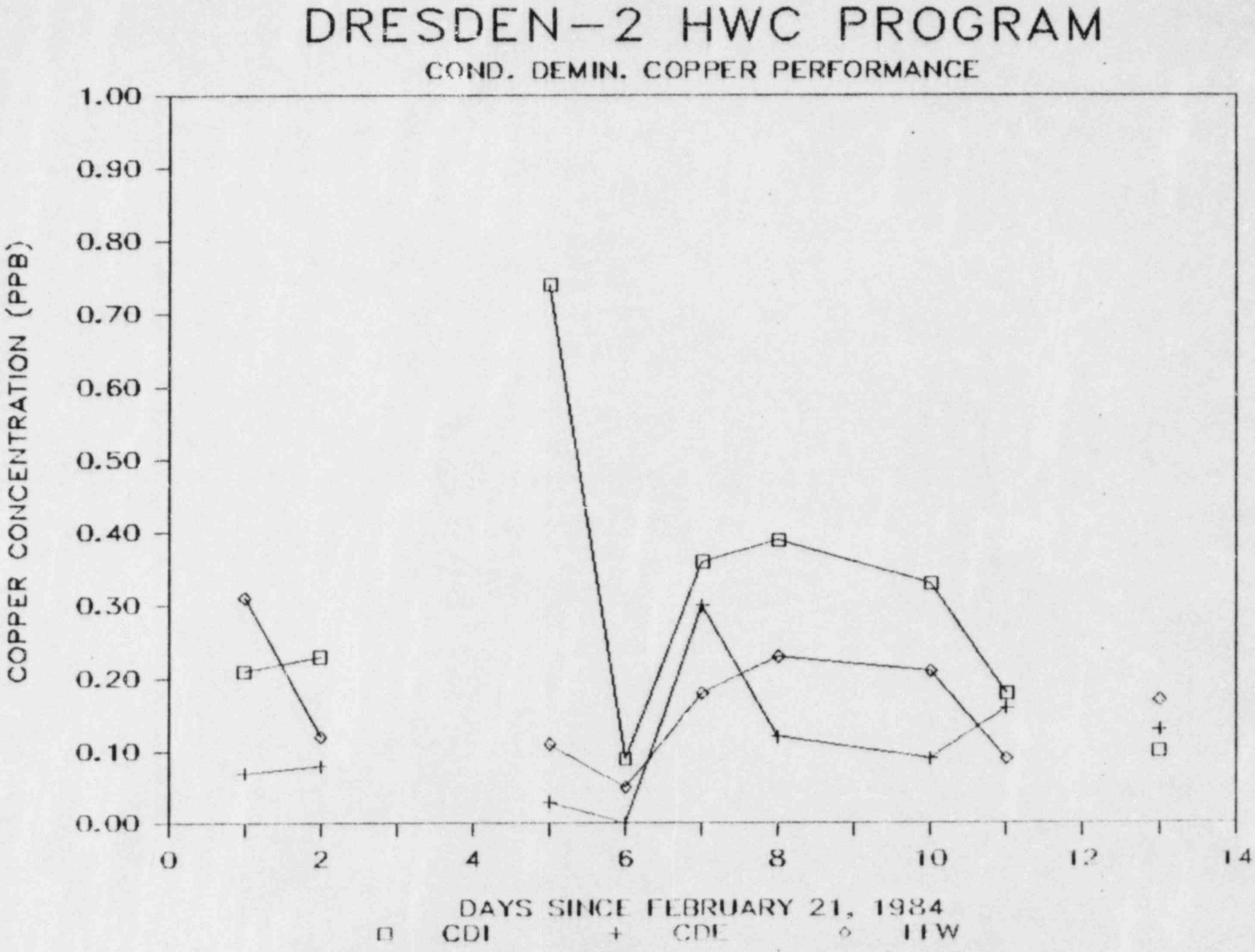
COND. DEMIN. CHLORIDE PERFORMANCE



DRESDEN—2 HWC PROGRAM

COND. DEMIN. SULFATE PERFORMANCE

FIGURE 9



DRESDEN-2 HWC PROGRAM

COND. DEMIN. COPPER PERFORMANCE

Table 1. CDI Ionic Impurity Concentrations (ppb).

DATE	TIME	CU	NI	ZN	NA	CL	SO4
22284	1100	0.21	0.17	1.88	2.42	3.03	2.34
22384	1100	0.23	0.32	1.80	3.31	4.03	0.93
22484	1500				0.98	1.91	1.09
22684	1300	0.74	0.28	1.58	1.12	0.98	1.49
22784	1115	0.09	0.05	1.43	0.80	0.81	0.98
22884	1200	0.36	1.09	1.75	0.30	0.54	1.79
22984	1130	0.39	0.56	1.53	5.24	5.76	2.69
30284	1045	0.33	0.65	2.05	1.42	1.59	1.93
30384	1045	0.18	0.62	1.40	0.64	0.72	2.35
30584	1045	0.10	2.38	4.46	1.01	1.26	0.89

Missing entries: No samples were collected.

Table 2. CDE Ionic Impurity Concentrations (ppb).

DATE	TIME	CU	NI	ZN	NA	CL	SO4
22284	1100	0.07	0.23	1.21	1.33	1.25	1.74
22384	1100	0.08	0.79	1.72	7.12	7.07	2.75
22484	1500				1.72	2.09	1.98
22684	1300	0.03	0.42	1.80	2.64	1.84	1.63
22784	1115	0.00	0.13	1.72	2.76	2.50	3.67
22884	1200	0.30	1.06	1.31	1.34	0.65	1.22
22984	1130	0.12	0.36	1.41	3.40	2.88	1.58
30284	1045	0.09	0.69	1.78	1.75	2.00	3.25
30384	1045	0.16	0.96	1.62	1.44	0.87	0.90
30584	1045	0.13	1.49	2.67	1.24	0.77	2.64

Missing entries: No samples were collected.

Table 3. FFW Ionic Impurity Concentrations (ppb).

DATE	TIME	CU	NI	ZN	NA	CL	SO4
22284	1100	0.31	0.24	2.32	1.24	1.13	1.51
22384	1100	0.12	0.45	1.98	2.25	2.26	0.93
22484	1500				1.21	1.41	2.59
22684	1300	0.11	0.89	2.04	1.03	0.51	3.08
22784	1115	0.05	0.24	1.71	2.82	3.21	1.84
22884	1200	0.18	1.32	1.03	1.04	0.64	1.61
22984	1130	0.23	0.53	1.41	3.65	1.16	1.38
30284	1045	0.21	1.20	2.08	0.94	0.42	0.75
30384	1045	0.09	1.03	1.83	0.54	0.10	0.85
30584	1045	0.17	1.05	1.23	0.86	0.77	1.91

Missing entries: No samples were collected.

within 0.02 min of the copper standard. Ferrous iron peaks, which elute relatively late compared to the other species were not observed in any samples. Potassium and ammonium ions were also not observed in any samples, nor were nitrate, nitrite, or oxalate anions. Perhaps these could have been detected using larger samples sizes, or a more sensitive detector attenuation. With the configuration used in this test, the concentration of each species is estimated to be less than 0.1 ppb. In a previous study at Dresden-2, the oxalate ion, or some species that elutes with the same retention time as oxalate, was observed in many stages of extraction steam and most primary system samples. The potassium ion is not normally encountered in BWR chemistry. Somewhat surprising was the absence of the common nitrogenous ions in CDI water, or reactor water samples (discussed later).

Figures 6 through 9 show the performance of the condensate treatment system (CDI vs. CDE) in the removal of sodium, chloride, sulfate, and copper. The feedwater concentration is also plotted to trend the release or plateout of metallic impurities along the feedwater train (CDE vs. FFW). In many cases, the effluent concentration (CDE) of each ion is greater than the concentration of the demineralizer inlet (CDI). If these data are real, it indicates the condensate demineralizers are sloughing impurities. If there were no net deposition or release of impurities down the feedwater train, the concentration of each species in the condensate demineralizer effluent and the final feedwater sample streams should be the same. The figures indicate that the CDE and FFW trend lines cross one another on several occasions, favoring neither the release or deposition mechanism.

To the best of our knowledge, the concentrations of sodium and sulfate have never been measured in the Dresden-2 reactor. The logical source of these ions in the condensate-feedwater train is the condensate demineralizer ion exchange resins, as sulfuric acid and sodium hydroxide are the regenerant chemicals. Hotwell sources (CDI) include inputs from the condensate storage tank and radwaste. Chloride concentrations in these streams are rarely monitored: usually, lower limits of detection (<20 ppb) are reported. The Dresden reactors should have low concentrations of chloride throughout the system, owing to the non-saline cooling water source.

Copper and nickel are routinely monitored in the feedwater as a requirement of the Fuel Warranty Operating Limits. In addition, General Electric has been sampling feedwater corrosion products on a continuous basis for the entire cycle of operation on hydrogen water chemistry. Soluble metallic impurity samples are collected on ion exchange membranes, using sample volumes on the order of 300 l. These measurements show an average copper concentration of 0.1 ppb, with occasional spikes approaching 0.3 ppb. Thus, the copper concentrations reported by the two methods are in reasonable agreement. Feedwater soluble nickel concentrations reported by the ion exchange membrane technique are on the order of 0.05 to 0.10 ppb, an order of magnitude below the concentrations determined by the ion chromatograph. A part of the problem for the nickel determination may be the stainless steel heads in the Eldex sample pumps, or some other stainless steel surface between the pump and the ion chromatograph concentrator column. The concentration of soluble zinc in feedwater using ion exchange membrane filters ranges between 0.01 and 0.02 ppb. This is nearly two orders of magnitude below the concentrations reported by the ion chromatograph. All three sample streams, CDI, CDE, and FFW, show zinc concentrations between 1 and 2 ppb on a routine basis. The concentration of zinc in the reactor water cleanup inlet and effluents, discussed in the next section, is also typically 1-2 ppb. This strongly suggests that a fixed level of zinc contamination was being introduced to each sample. The source of this zinc contamination is under investigation.

Figure 10 shows the conductivity readings for these three process streams during the time periods when samples were acquired for the ion chromatograph analyses. Here it appears that the condensate demineralizers are doing an effective job in the removal of impurities, with the average removal efficiency on the order of 70%. pH measurements were not made on these sample streams, and the actual removal efficiency of impurities may be somewhat greater, if the inlet or effluent pH is slightly different than 7.00. In most cases, the final feedwater conductivity is greater than the condensate demineralizer effluent conductivity, perhaps indicating a solublization of impurities down the feedwater train.

Table 4 compares the conductivities from the three process instruments with the calculated conductivities, which are based on the sum of the equivalent conductances of the separate ions, Na, Cl, SO_4, Cu, Ni, and Zn, at infinite dilution. The calculated sums also include the contribution of theoretically pure water, 0.0550 uS/cm at 25°C, having a pH of 7.00.

FIGURE 10

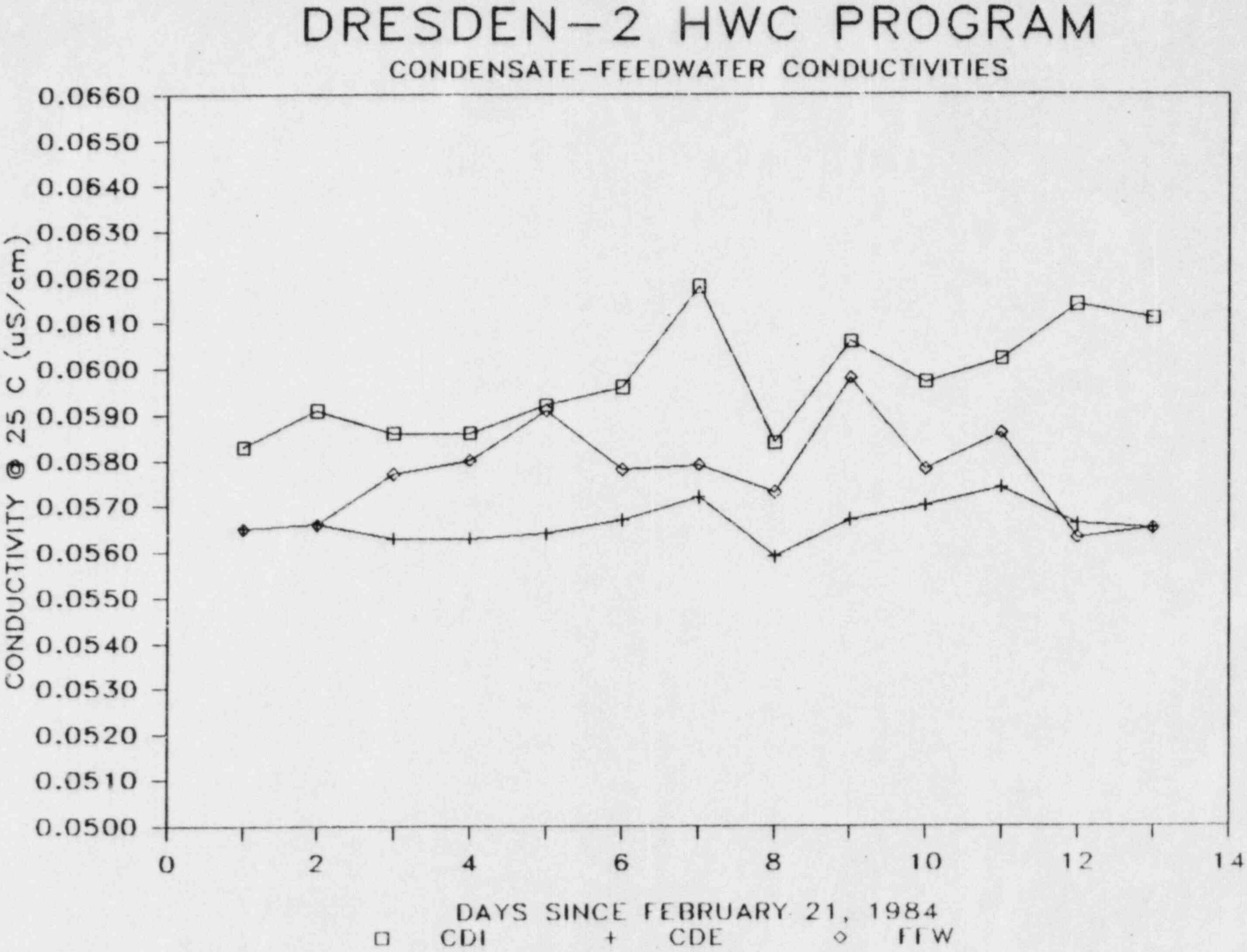

DRESDEN-2 HWC PROGRAM
CONDENSATE-FEEDWATER CONDUCTIVITIES
CONDUCTIVITY @ 25 C (uS/cm)
0.0660
0.0650
0.0640
0.0630
0.0620
0.0610
0.0600
0.0590
0.0580
0.0570
0.0560
0.0550
0.0540
0.0530
0.0520
0.0510
0.0500
0
2
4
6
8
10
12
14
DAYS SINCE FEBRUARY 21, 1984
□ CDI
+ CDE
◇ FFW

Table 4. Condensate-Feedwater Conductivities (uS/cm).

DATE	TIME	CDI IONCHROM	CDI METER	CDE IONCHROM	CDE METER	FFW IONCHROM	FFW METER
22284	1100	0.0744	0.0583	0.0659	0.0565	0.0673	0.0565
22384	1100	0.0763	0.0591	0.0946	0.0566	0.0705	0.0566
22484	1500	0.0630	0.0586	0.0665	0.0563	0.0650	0.0577
22584	1100		0.0586		0.0563		0.0580
22684	1300	0.0663	0.0592	0.0711	0.0564	0.0685	0.0591
22784	1115	0.0627	0.0596	0.0755	0.0567	0.0744	0.0578
22884	1200	0.0651	0.0618	0.0658	0.0572	0.0655	0.0579
22984	1130	0.0874	0.0584	0.0743	0.0559	0.0713	0.0573
30184	1200		0.0606		0.0567		0.0598
30284	1045	0.0697	0.0597	0.0727	0.0570	0.0649	0.0578
30384	1045	0.0655	0.0602	0.0660	0.0574	0.0627	0.0586
30484	1200		0.0614		0.0566		0.0563
30584	1045	0.0728	0.0611	0.0708	0.0565	0.0658	0.0565

In every set of paired measurements, the conductivity as read from the process instrument is less than the calculated conductivities from the ion chromatograph measurements. This again suggests that the samples might be picking up some contamination between acquisition and analysis. The contamination might originate from the atmosphere, handling operations, or perhaps from some internal components of the instrument.

None of the condensate-feedwater ionic impurity measurements appear to correlate with the on or off status of the hydrogen addition system. The dissolved hydrogen concentration in the CDI and CDE sample streams is less than 2 ppb with or without hydrogen addition. The hydrogen is injected into the condensate booster pumps, located downstream of the condensate demineralizers. Hydrogen carried over with the steam is recombined in the offgas treatment system. The concentration of dissolved oxygen in the condensate-feedwater train is reduced as a result of hydrogen addition, because less oxygen is carried over with the steam, resulting in a lower equilibrium concentration in the condenser. No ionic effects were observed in the final feedwater (ca. 1 ppm H_2 with hydrogen addition, 2 ppb without) during the measurement period. Any changes that are occurring might be evident only in a long-term testing program.

Reactor Water Results

Tables 5 through 7 show the concentrations of ionic impurities as measured by the ion chromatograph in the RCI, RCEA, and RCEB sample streams, respectively.

It was somewhat surprizing that nitrate, nitrite, and ammonium ions were not detected in the reactor water samples. If present, their concentrations are estimated to be less than 0.1 ppb. Perhaps this implies that the dominant forms of nitrogen in a reactor are gaseous molecules, either N^2, NO, or NO^2. The concentrations of sodium and sulfate ions have never been measured in reactor water prior to this campaign. Previous chloride measurements at the Dresden-2 reactor again suffer from the lack of measurement sensitivity. Concentrations of less than 20 ppb are typically reported. Station personnel do not measure the concentration of transition metals in reactor water. The General Electric sampling program measures the transition metals in reactor water, as taken from the reactor water recirculation sample point, but no monitoring is performed on either effluent from the cleanup system. Ion exchange filter samples are collected three times per week, typically with 10-liter volumes. By this technique, the average copper concentration in the reactor water is 1 ppb, with occasional spikes up to 4 ppb. For copper, the ion chromatography data are in reasonable agreement with the filter samples. We have previously reported soluble nickel concentrations in reactor water that range between 0.1 and 0.2 ppb. These values are roughly a factor of five lower than the ion chromatography measurements, and again we suspect sample contamination by the system. The reactor water zinc measurements by the ion chromatograph are an order of magnitude higher than results using the filter technique (1.5 vs. 0.15 ppb).

Figures 11 through 14 show the concentrations of sodium, chloride, sulfate, and copper as a function of time for the reactor water cleanup system inlet and effluents. There is a strong correlation between the concentration of sodium in the reactor water (Figure 11), and the reactor water conductivity and power (Figure 1). The data indicate that at full power, a 90% removal efficiency for sodium is achieved. For all four species, the concentrations in the "A" and "B" effluents are comparable, indicating similar removal efficiencies for each cleanup demineralizer. No correlation was found between the concentration of any species measured by the ion chromatograph and the on or off status of the hydrogen addition system. Sodium and chloride ions, each having only one common valence state, should not be affected

Table 5. RCI Ionic Impurity Concentrations (ppb).

DATE	TIME	CU	NI	ZN	NA	CL	SO4
22284	1100	0.37	0.22	1.83	2.25	3.40	2.91
22384	1100	0.90	0.77	3.02	6.34	3.89	1.66
22484	1500				4.05	2.35	2.51
22684	1300	0.75	0.62	2.21	6.31	3.04	4.21
22784	1115	0.67	0.21	1.21	12.80	4.50	3.51
22884	1200	1.38	1.31	1.42	11.40	1.68	3.05
22984	1130	0.86	0.70	1.40	14.40	2.65	3.27
30284	1045	0.62	0.81	1.57	10.10	1.23	1.93
30384	1045	0.49	0.74	2.06	10.20	1.92	3.12
30484	1200	1.67	0.68	5.11	10.40	17.3	2.96
30584	1045	0.90	1.32	1.58	10.80	7.85	2.30

Missing entries: No samples were collected.

Table 6. RCEA Ionic Impurity Concentrations (ppb).

DATE	TIME	CU	NI	ZN	NA	CL	SO4
22284	1100	0.08	0.03	1.48	0.29	0.00	1.40
22384	1100	0.11	0.56	2.33	1.01	1.49	0.85
22484	1500				1.29	2.42	1.01
22684	1300	0.12	0.40	1.85	0.76	0.59	1.45
22784	1115	0.05	0.21	1.14	1.71	2.14	1.18
22884	1200	0.15	1.07	0.71	0.92	0.96	1.79
22984	1130	0.09	0.69	1.60	1.39	1.18	1.50
30284	1045	0.02	0.76	2.11	0.76	1.03	0.75
30384	1045	0.09	1.18	1.33	0.49	0.27	1.20
30584	1045	0.15	0.77	1.36	0.43	0.77	1.06

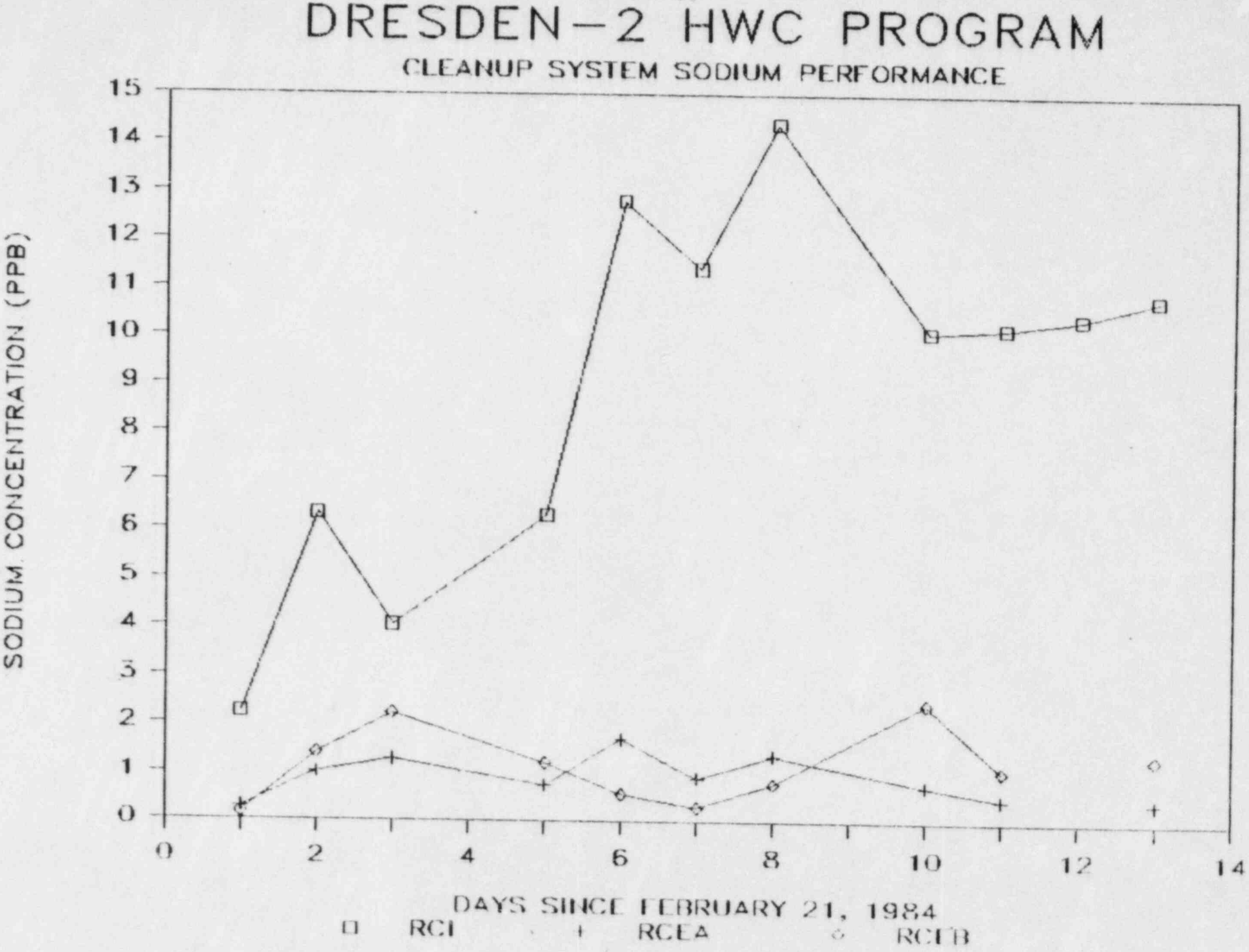
Missing entries: No samples were collected.

Table 7. RCEB Ionic Impurity Concentrations (ppb).

DATE	TIME	CU	NI	ZN	NA	CL	SO4
22284	1100	0.07	0.11	1.33	0.17	0.00	0.91
22384	1100	0.11	0.72	2.59	1.41	2.11	0.81
22484	1500				2.24	3.80	1.21
22684	1300	0.13	0.20	1.86	1.22	0.78	1.22
22784	1115	0.09	0.00	1.53	0.57	0.94	0.94
22884	1200	0.21	0.79	1.21	0.30	0.60	2.62
22984	1130	0.14	0.49	1.13	0.80	0.96	1.04
30284	1045	0.17	0.76	8.60	2.46	3.23	0.80
30384	1045	0.01	1.03	5.87	1.08	1.20	0.98
30584	1045	0.20	1.13	1.59	1.35	2.27	1.02

Missing entries: No samples were collected.

FIGURE 11


DRESDEN-2 HWC PROGRAM
CLEANUP SYSTEM SODIUM PERFORMANCE
SODIUM CONCENTRATION (PPB)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
2
4
6
8
10
12
14
DAYS SINCE FEBRUARY 21, 1984
□ RCI
+ RCEA
◇ RCEB

DRESDEN-2 HWC PROGRAM

CLEANUP SYSTEM CHLORIDE PERFORMANCE

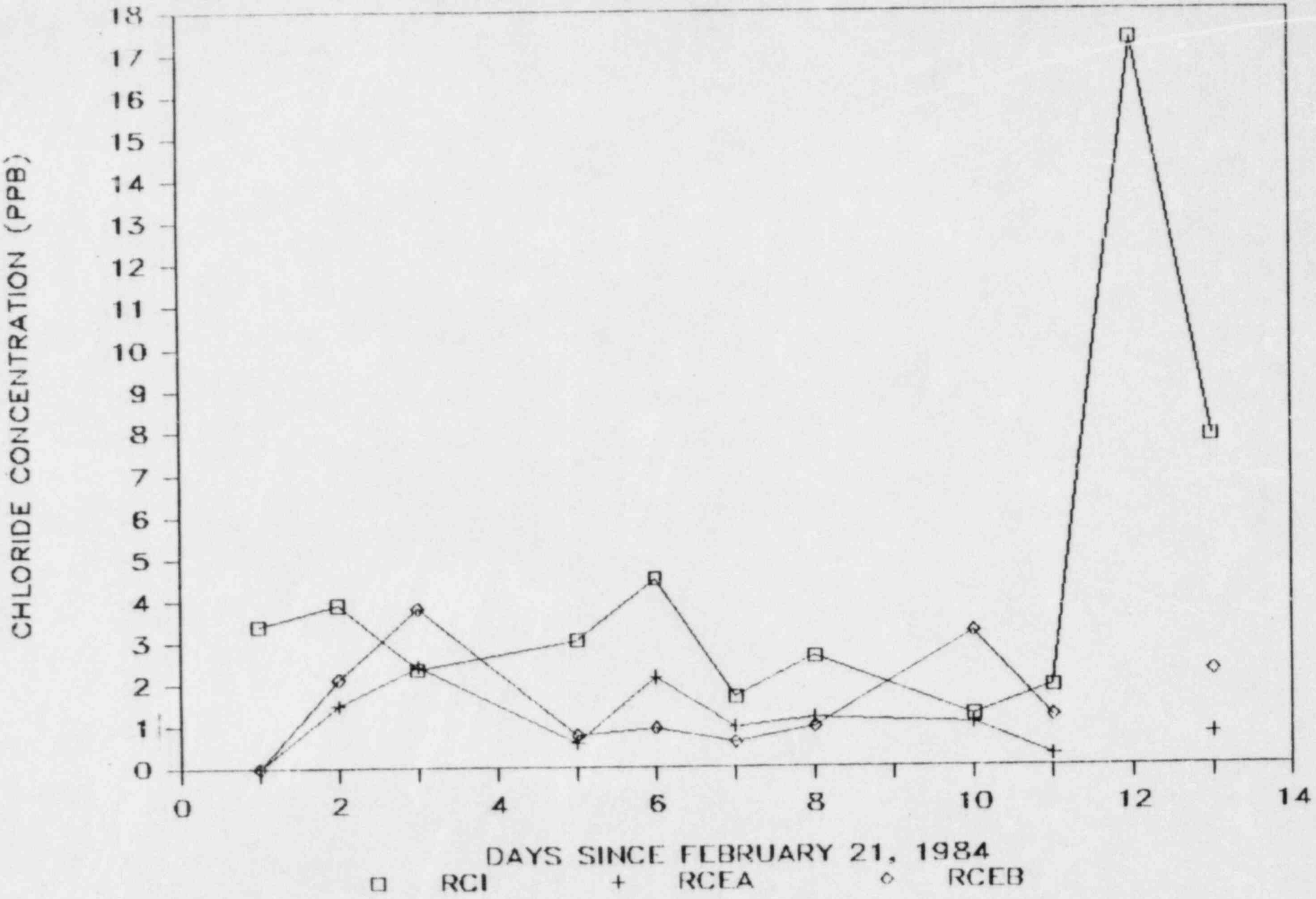
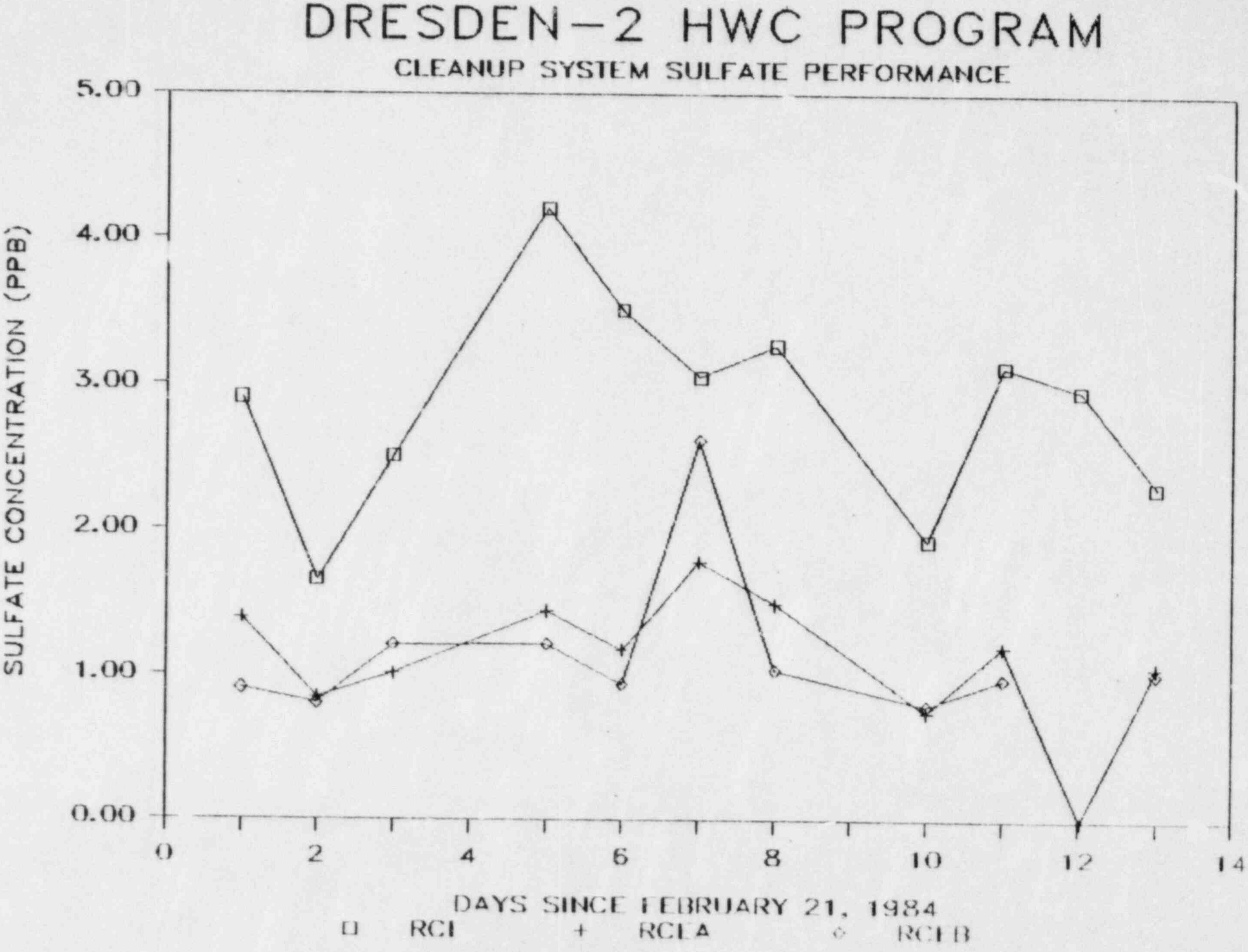
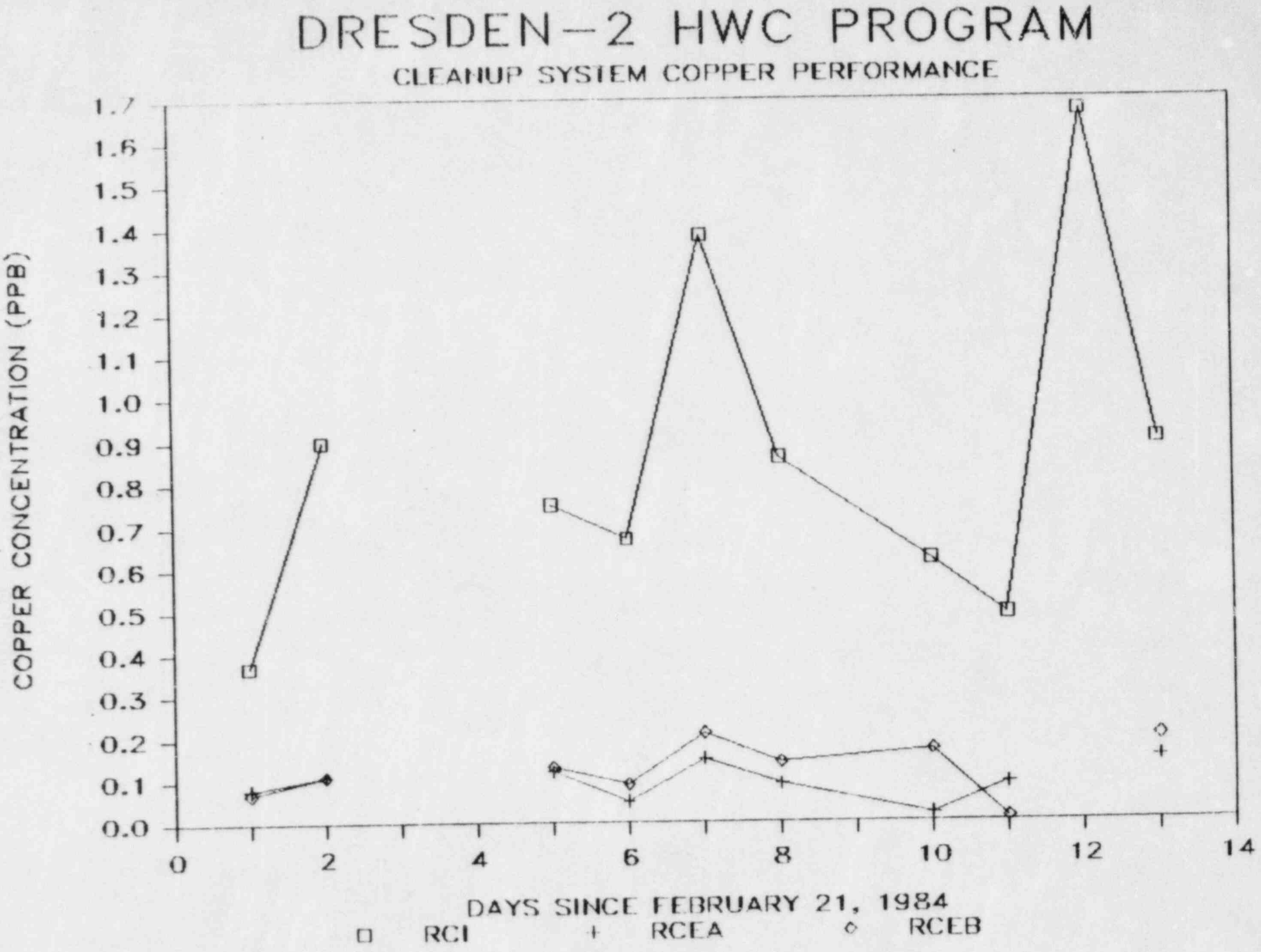


FIGURE 13


DRESDEN-2 HWC PROGRAM
CLEANUP SYSTEM SULFATE PERFORMANCE
SULFATE CONCENTRATION (PPB)
5.00
4.00
3.00
2.00
1.00
0.00
0
2
4
6
8
10
12
14
DAYS SINCE FEBRUARY 21, 1984
□ RCI
+ RCEA
◇ RCEB



DRESDEN-2 HWC PROGRAM

CLEANUP SYSTEM COPPER PERFORMANCE

by the oxidation-reduction characteristics of the core. The sulfate ion could possibly be reduced to some lower valent species, but no spurious peaks in the chromatograms were observed, nor did the retention time of the eluting sulfate ion shift on a day-to-day basis. There is no strong evidence that the concentrations of copper, nickel, or zinc are being affected by hydrogen addition.

In spite of the possibility of sample contamination, we again have attempted to reconcile the reading from the reactor water process conductivity monitor with the sum of the conductivities obtained from the ion chromatograph, using the equivalent conductances of the separate ions at infinite dilution. These data are shown in Table 8.

Table 8. Reactor Water Conductivity Balance.

DATE	TIME	RCI PH	INSTRUMENT CONDUCTIVITY (uS/cm)	CHROMATOGRAPH CONDUCTIVITY (uS/cm)
22284	1100	6.67	0.076	0.105
22384	1100	7.07	0.076	0.086
22484	1500	7.17	0.099	0.071
22684	1300	7.00	0.092	0.088
22784	1115	7.30	0.129	0.104
22884	1200	7.25	0.123	0.095
22984	1130	7.10	0.115	0.100
30284	1045	7.16	0.121	0.086
30384	1045	7.44	0.126	0.104
30484	1200	6.50	0.147	0.194
30584	1045	7.25	0.107	0.106

The chromatography conductivity column in the above table includes the contributions from hydroxide and hydrogen ions which were obtained from the pH measurements. In the reactor water, we see several instances where the process instrument conductivity is higher than the sum of the individual ionic contributions. In most cases, the process instrument value is higher when the indicated conductivity is greater than 0.1 uS/cm. This is reasonable in that the contributions of the various contaminants to the sample are less when the actual impurity concentration is increased. With calibrated process instrument meters, cells, and temperature indicators, and appropriate temperature compensation of the conductivity readings, the use of the equivalent conductances of the separate ions provide a good cross check on the adequacy of the ion chromatograph measurements.

A second cross check of the ion chromatography measurements is a summation of the cation and anion equivalents in the sample: this requires the additional measurement of pH, since the ion chromatograph does not detect hydrogen or hydroxyl ions. If the ion chromatograph is accounting for all the ionic impurities in solution, the number of cation equivalents should equal the number of anion equivalents. The results of this excercise are shown in Table 9.

Table 9. Cation/Anion Equivalents Balance.

DATE	TIME	CATION EQUIV	ANION EQUIV	CAT-AN EQUIV	HCO_3- PPB	SUM COND. uS/cm	METER COND. uS/cm
22284	1100	3.87E-07	2.03E-07	1.83E-07	11.2	0.113	0.076
22384	1100	5.08E-07	2.62E-07	2.46E-07	15.0	0.097	0.076
22484	1500	2.44E-07	2.66E-07	--------	----	0.070	0.099
22684	1300	4.87E-07	2.73E-07	2.13E-07	13.0	0.098	0.092
22784	1115	6.72E-07	4.00E-07	2.72E-07	16.6	0.116	0.129
22884	1200	6.83E-07	2.89E-07	3.95E-07	24.1	0.113	0.123
22984	1130	7.99E-07	2.69E-07	5.30E-07	32.4	0.124	0.115
30284	1045	6.03E-07	2.19E-07	3.84E-07	23.4	0.103	0.121
30384	1045	5.83E-07	3.95E-07	1.89E-07	11.5	0.113	0.126
30484	1200	1.00E-06	5.81E-07	4.19E-07	25.6	0.213	0.147
30584	1045	6.47E-07	4.47E-07	2.00E-07	12.2	0.115	0.107

The cation equivalents represent the sum of sodium, hydrogen, nickel, copper, and zinc ions, while the anion equivalents represent the sum of chloride, sulfate, and hydroxide ions. With one exception, all the measurements show a significant anion deficiency. Because the anion eluent used for these measurements is a mixture of carbonate and bicarbonate ions, the concentrations of these species could not be measured. The most logical sources of these ions in the BWR are condenser air inleakage, where carbon dioxide hydrolyzes to carbonic acid, which then breaks down to bicarbonate and carbonate ions, and the decomposition of organic matter to carbon dioxide, followed by the same hydrolysis and equilibrium dissociation reactions. We have ascribed the equivalents difference totally to the bicarbonate ion, owing to the neutral pH of the water. The carbonate ion would make a greater contribution at higher pH values. This somewhat crude method shows the concentration of reactor water bicarbonate ion ranges between 10 and 30 ppb. The addition of the bicarbonate conductivity contribution to the sum obtained using the equivalent conductances of the separate ions makes the agreement with the process conductivity meter somewhat better for those cases where the meter reading was originally higher.

Recommendations for Future Studies

In spite of all the precautions that were taken for this study, there is strong evidence that many samples suffered from contamination, either in the acquisition, analysis, or both facets of the determination. Contamination has been, and always will be the Achilles heel of grab sampling characterizations at the part per billion level. Using the automatic sample changers that were designed for this test, sample lines should be hard piped directly to the rotary valve ports, with additional valving provided to accomodate high velocity bypass flow immediately upstream of the sample changer. Sample contact with fresh metallic surfaces should be minimized. Sample pump heads should be fabricated from Kel-F or some other inert, non-leaching material: incoming sample lines should be Teflon as much as possible. At Dresden-2, hard piping of sample lines will require that two separate instrument packages be provided, since condensate/feedwater sample lines are located in the turbine building, and reactor water cleanup sample lines are located in the reactor building. This configuration would permit more sample analyses per day on any given stream, and provide a better opportunity to detect transients in a timely fashion, should they occur.