GPU Nuclear	TDR NO. _341_	REVISION NO. _0_
TECHNICAL DATA REPORT	BUDGET ACTIVITY NO. _120010_	PAGE ____ OF ____

PROJECT:	DEPARTMENT/SECTION _OTSG Failure Analysis_
TMI-1	RELEASE DATE _____ REVISION DATE _____

DOCUMENT TITLE:

TMI-1 OTSG Failure Analysis Report

ORIGINATOR SIGNATURE	DATE	APPROVAL(S) SIGNATURE	DATE
J. D. Jones		R. L. Long	
R. L. Jones (EPRI)		D. G. Slear	
J. S. Olszewski (B&W)			
		APPROVAL FOR EXTERNAL DISTRIBUTION	DATE
		R. F. Wilson	

*	DISTRIBUTION	ABSTRACT:

DISTRIBUTION

R. L. Long
J. D. Jones
R. L. Jones
J. S. Olszewski
R. F. Wilson
D. G. Slear
F. S. Giacobbe
M. J. Graham

ABSTRACT:

Statement of Problem

Investigate the failure of the OTSG tubes to identify the damage mechanism.

Key Results

1. OTSG tube cracks were I.D. initiated.
2. Sulfur was present on crack surfaces.
3. Analysis of primary coolant revealed the presence of sulfur.
4. Sulfur has been shown to promote intergranular stress assisted cracking (IGSAC) in OTSG tube material.

5. Aggressive sulfur species formed subsequent to hot functional testing and cracked the OTSG tubes during cooldown or cold shutdown.

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I. EXECUTIVE SUMMARY

A. Failure Analysis Task Group

The Failure Analysis Task Group was organized as Task 1 of the Once Through Steam Generator Project Team. The principal purpose of Task 1 was to identify the cause of the TMI-1 Once Through Steam Generator (OTSG) tube damage mechanism. The group was then to develop recommendations for passivation and cleanup and prevention of the damage mechanism occurring again.

The Failure Analysis Task Group was organized under the direction of R. L. Long and included individuals from a variety of organizations within GPUN. Table I-1 indicates the key responsible individuals from GPUN.

A similar Failure Analysis Task Group was organized at Babcock & Wilcox under the direction of J. S. Olszewski and key individuals in this group are shown in Table I-2.

As noted in Table I-1, Dr. Robin Jones of the Electric Power Research Institute, Systems & Materials Group, also was an active participant in the Failure Analysis Task Group.

B. Report Purpose and Organization

The purpose of this report is to present the findings of the Failure Analysis Task Group. Section II of the report presents a brief description of the Once Through Steam Generator (OTSG) as a basis for subsequent discussions and a summary description of the intergranular stress assisted attack phenomena observed in the OTSG's, following the discovery of primary to secondary leakage in November, 1981.

Sections III and IV present Operational and Chemistry history, respectively. The results of a fairly extensive sampling program implemented after the November 1981 discovery is included in Section V. In Section VI, the results of the detailed metallurgical examinations of tube samples pulled from the TMI-1 OTSG's are described.

Section VII presents a summary of the detailed information that has been gathered regarding the fabrication history of the OTSG's. In Section VIII the results of tube stress analyses, performed primarily by MPR, Incorporated, are presented. Section IX describes the results of cracking testing which has been underway, attempting (1) to demonstrate the conditions which caused the attack, (2) to verify that cracks are no longer propagating and (3) to test the validity of the passivation and cleanup proposals.

Finally, Section X delineates the postulated cause of failure and the recommendations coming out of the Failure Analysis Group.

C. Findings

1. History

   a. Fabrication History

      The fabrication history of the TMI-1 OTSG's is typical of such Babcox and Wilcox units. There is no indication that tube material, fabrication or installation in the OTSG's was in any way extraordinary. The heat treatment of the whole OTSG following assembly has the effect of sensitizing the tube material to possible intergranular attack. This is common to all OTSG's manufactured by this process. Reference 2 reports the details of the fabrication history.

   b. Operational History

      The operational history of the TMI-1 OTSG's reveals no subjection of the tubes to excessive stress during the time when damage occured.

      Operations did, however, have a significant impact on the chemical environment of the OTSG tube. There were five (5) identifiable instances of probable intrusion of chemical contaminants into the Reactor Coolant System (RCS). In March 1979, oil was introduced into the reactor coolant bleed tanks, probably by overflowing the miscellaneous waste storage tank through the vent header. Some oil may subsequently have found its way into the RCS. In October 1979, sulfuric acid was injected into the reactor coolant makeup system. Although attempts were made to prevent the acid from reaching the RCS, chemistry results indicate some contamination of the RCS occurred. In July 1980, May 1981, and September 1981, there are indications that sodium thiosulfate from the building spray system found its way into the RCS.

      Significant to the localization of the attack was the history of the water level on the primary side of the OSTG. Figure I-1 shows water level as a function of time. It is noteworthy that following the hot functional testing in September 1981, water level was promptly lowered then slowly raised over several days. This allowed a drying then rewetting of the tubes in the upper portion of the steam generator. Reference 1 reports the details of the operational history.

2. Metallurgical Results

   a. Analysis Program

      A multi-task program was planned to provide information related to the steam generator tube damage problem. This program contained the following analyses/examinations:

1) Visual Examination

2) Eddy-Current Examination

3) Radiography

4) Sectioning and Bending

5) Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDAX)

6) Auger Electron Spectroscopy (AES)

7) Electron Spectroscopy for Chemical Analysis (ESCA)

8) Sodium Azide Spot Test

9) Metallography-Microstructural Analysis

10) STEM, EPR and Huey Testing

11) Residual Stress and Plastic Strain

12) Tension Testing

13) Hardness Testing

14) Dimensional Measurements

b. Test Program Results/Conclusions

The detailed test results are presented in Section VI. The following summarizes those results and sets forth some conclusions:

1) The tubing failed due to stress assisted intergranular attack. This lead to through wall penetrations and circumferentially oriented cracks. In all cases, cracks were initiated on the inside surface.

2) The intergranular morphology has been confirmed by both Metallography and Electron Microscopy.

3) Transmission Electron Microscopy has also confirmed that no secondary modes of failure are associated with the intergranular corrosion, that is, no evidence of any low or high cycle fatigue was observed on these fracture surfaces.

4) In conjunction with the cracking, there has also been general intergranular attack observed. In general, this has been characterized as severe by Battelle Columbus and has

been characterized as not severe by B&W. The differences between the two laboratories is most likely associated with the extent of severity of the cracks observed at the locations where intergranular attack was noted. More severe cracking, in general, relates to more severe intergranular attack.

5) Analysis of surface films on fracture surfaces and on the I.D. surface of the tubing indicate that sulfur is present up to levels of eight (8) atomic percent, and that it is this sulfur that is most likely responsible for the cracking phenomena. Although the form of sulfur has not been definitively determined, it is believed to be either in the form of a nickel sulfide, $Ni_2 S_3$ or some other reduced form of sulfur. It is believed that the presence of the reduced sulfur form is responsible for the cracking mechanism and without such a contaminant the attack would not have occurred.

6) Microstructural evaluation of the tubing from numerous locations, has indicated that the structure is representative of that normally expected for steam generator tubing. However, tests have concluded that the material is in a sensitized condition, and hence, is expected to be susceptible to intergranular attack.

7) Visual, metallographic or bend specimens performed in clean regions of the tubing, that is regions where the standard differential eddy-current probe operates and no eddy-current indications were recorded, all show the tubing to be free of defect. In addition, all examinations performed at locations where absolute eddy-current probing indicated a nearly through wall or through wall defect has confirmed the presence of cracking in those regions. Comparisons of metallographic and eddy-current results have generally shown a one-to-one correlation. In the seal weld Heat Affected Zone (HAZ) where due to tube end effects the standard differential probe is ineffective, defects were first detected visually, then confirmed by absolute probe.

8) Although there is excellent correlation between eddy-current indications and metallography, it has also been learned that eddy-current signals of 80% to 90% through wall, in most instances actually represent a 100% through wall defect.

9) In all cases to date, cracks which have been examined either by metallography or by bend testing, have shown the defects to be at least 90% and generally 100% through wall in penetration. No defects in the range of 10% to 50% have been observed. This would suggest that crack growth rates

are rapid and that defects, once initiated, propagate through wall. Some eddy-current indications in the 50% - 90% through wall range have been observed.

10) Auger and ESCA analysis have shown the presence of carbon, nickel, chromium, oxygen and sulfur on the fracture surfaces. In addition, normal trace quantities of fission products have also been observed. The important results from this analysis have shown that sulfur concentrations along the I. D. surface of the tubing down to the 27 inch point, are generally uniform with perhaps a slightly decreasing level as you go down the tube length. In addition, the large presence of oxygen also confirms that oxygen was definitely available for the cracking reactions and very possibly played a major roll for the failures observed.

11) The consistent circumferential orientation of the cracks indicates that a longitudinal stress is part of the cracking mechanism. Residual stresses in the roll alone were not responsible for the cracking.

3. Chemistry Results

Generally, the reactor coolant system remained within specifications for those parameters for which an analysis requirement existed for the period extending from April 1979 through November 1981. Two incidents of intrusion of ionic substances not accounted for by specific analyses have been identified. Sodium thiosulfate at levels of 4-5 ppm as thiosulfate is considered to be the most likely contaminent. The ionic species from the first contamination incident in July 1980 were removed from the bulk liquid by demineralization in August 1980. The ionic species from the second contamination incident in May 1981 appear to have been only partly removed by processing through a resin water precoat filter in August 1981. A 1-2 ppm thiosulfate residual could have still been present at the start of September 1981. The operational history shows that additional sodium thiosulfate in the RCS may have resulted from injections of Borated Water Storage Tank (BWST) contents during cooldown from hot functional testing. The quantity was not sufficient to be detectable by conductivity. Induction of an unidentified organic substance, probably oil or grease, into RCS auxiliary systems occurred in mid-March 1979. The exact quantity of this substance or its potential role in the failure mechanism has not been established. It has been determined that this substance could not have introduced sulfur into the RCS in the quantities observed. Details are provided in Reference 1.

4. Distribution of Damage

In-situ eddy-current results exhibit tube wall defect indications at varied rates distributed both axially and radially in both OTSG 'A' and 'B' tube bundles. The majority of the defect indications are in the upper tubesheet (UTS) region and particularly confined to the tube roll transition zone. Ninety-five (95) percent of all tubes with defect indications are contained in the top seven (7) inches of UTS with less than 200 tubes containing defect indications below the UTS (80 percent of those defects are above the top support plate). Radial distribution of tubes with defect indications in 'A' OTSG shows a high percentage in the UTS periphery with the defect rate decreasing rapidly as you move toward the center of the bundle. In the 'B' OTSG, however, half of the UTS exhibits an approximate 20 percent defect rate with defect rates to 90 percent in a broader peripheral area of the other half. Reference 9 documents defect rates in detail.

5. Damage Scenario

The occurrence of stress assisted cracking requires that three (3) conditions be satisfied simultaneously:

o   a sufficiently high tensile stress
o   a susceptible material microstructure
o   an aggressive environment

The information presented in subsequent sections of this report relating to these three (3) factors is summarized below:

a. Tensile Stress

Section VIII presents information about OTSG tubing stresses. Since the cracks are oriented circumferentially in the tubes, axial tensile stresses are of principal interest. Both operating and residual stresses must be considered since both can play a role in IGSCC (for example, both categories of stress are involved in IGSCC of BWR stainless steel piping). Cracking must have occurred in a situation in which the sum of the operating and residual stresses in the axial direction was greater than that in the hoop direction, otherwise the crack orientation would have been axial. The Section VIII analyses indicate that this condition is satisfied during cooldown and cold shutdown. Highlights of the stress analysis from the failure scenario viewpoint are:

1) Tubing axial tensile stresses are largest during cooldown when they may approach the yield stress.

2) Significant axial tensile stresses also exist during cold shutdown.

3) Locally high axial tensile stresses are possible in the seal weld heat affected zone and in the vicinity of the roll transition.

4) Under heatup and at full operating temperature the hoop stress generally is larger than the axial stress.

5) The axial stresses are generally larger at the periphery than in the center of the tube bundle.

Thus the stress analysis results suggest that the cracking must have occurred during cooldown or during cold shutdown. The stress analysis also explains why the seal weld heat affected zone and the roll transition region should be particularly prone to cracking and why more cracking occured in the periphery than in the center of the tube bundle.

b. Susceptible Material Microstructure

The OTSG fabrication history is documented in Section VII.

The fabrication history puts the tubing into service in the mill annealed plus stress relieved condition which is expected to be heavily sensitized (i.e., grain boundary chromium content less than 10%). Metallurgical examination has confirmed that the expected microstructure is present.

c. Aggressive Environment

The results presented in Section V indicate that sulfur was present in the primary system water and three (3) possible sources of sulfur have been identified from the OTSG chemistry history (Section IV).

If SO_4 and S_2O_3 were introduced to the primary water as the OTSG operating and chemistry histories suggest, they would be expected to persist as long as the water was at room temperature even if the oxygen content of the water was reduced by hydrazine additions. However, hydrogenating and heating the water to perform a hot functional would be expected to result in the generation of S^{--}, possibly accompanied by S and other intermediate species. Subsequent cooling to room temperature and oxygenating following the hot functional would rapidly oxidize S^{--} to S and could also result in the appearance of significant concentrations of other species of higher oxidation states. Although it is not possible to predict either the identities or the concentrations of the sulfur species present following the hot functional test, it is clear that this transient is likely to have greatly affected the aggressiveness of the environment with regard to low temperature sulfur-induced attack of the OTSG tubing.

6. Proposed Failure Scenario

The discussions presented above suggest that the probable cause of failure was as follows:

a. During lay up the primary system was contaminated with sulfur by the accidental introduction of sulfuric acid, sodium thiosulfate, and possibly a sulfur-containing oil. The amount of sulfur present may have reached several ppm, but the contaminated water was not aggressive enough to crack mill annealed plus stress relieved Alloy 600. Cracking tests confirm that cracking would not have been expected to occur at this stage.

b. The temperature and oxidation potential transient associated with the hot functional test resulted in a change in the types and concentrations of sulfur species present in the primary water. Further changes occurred when thiosulfate-contaminated water was injected during the tests of the high pressure and low pressure injection systems.

c. When the water level in the OTSGs was lowered following the hot functional test, high concentrations of aggressive metastable sulfur species developed in the dry-out region at the top of the generators due to the combined effects of solution concentration by evaporation and the comparatively high availability of oxygen. Changes in the sulfur species in the more dilute bulk solution proceeded more slowly resulting in lower concentrations of aggressive sulfur species.

d. Sulfur-induced IGSCC of the Alloy 600 tubing occurred rapidly in the dry-out zone with preferential attack at high stress locations. Little or no cracking occurred below the water line because the bulk solution was less aggressive.

e. Cracking terminated either because continued chemistry changes resulted in the formation of less aggressive sulfur species or because the environment in the dry-out region was diluted by the slowly-rising bulk solution. By the time the water level was dropped again, the chemical state of the sulfur in the primary water was sufficiently different from its state immediately after the hot functional to prevent a full scale recurrence of steps c. and d. in the new dry-out zone.

f. Cracking was discovered when the OTSG's were pressurized.

This scenario is consistent with all of the observed features of the cracking phenomenon (with the possible exception of the nonaxisymmetric radial distribution of cracking in OTSG-B) and is also consistent with the timing of the cracking and the results of the metallurgical examinations and corrosion tests.

7. Cracking Testing

Cracking testing to confirm the above scenario is currently being conducted. Preliminary observations are:

a. M2320 Archive Material appears less susceptible to cracking than actual generator tube material.

b. The presence of an inert atmosphere reduces cracking tendency.

c. Sulfate at low temperature will not cause cracking under oxidizing conditions.

d. Thiosulfate at low temperature will cause cracking under oxidizing conditions.

e. Archive Material in the mill-annealed and stress relieved condition has cracked in 5 ppm thiosulfate, but not in 1 ppm thiosulfate, indicating a threshold concentration requirement of greater than 1 ppm.

TABLE I-1
GPUN FAILURE ANALYSIS TASK GROUP

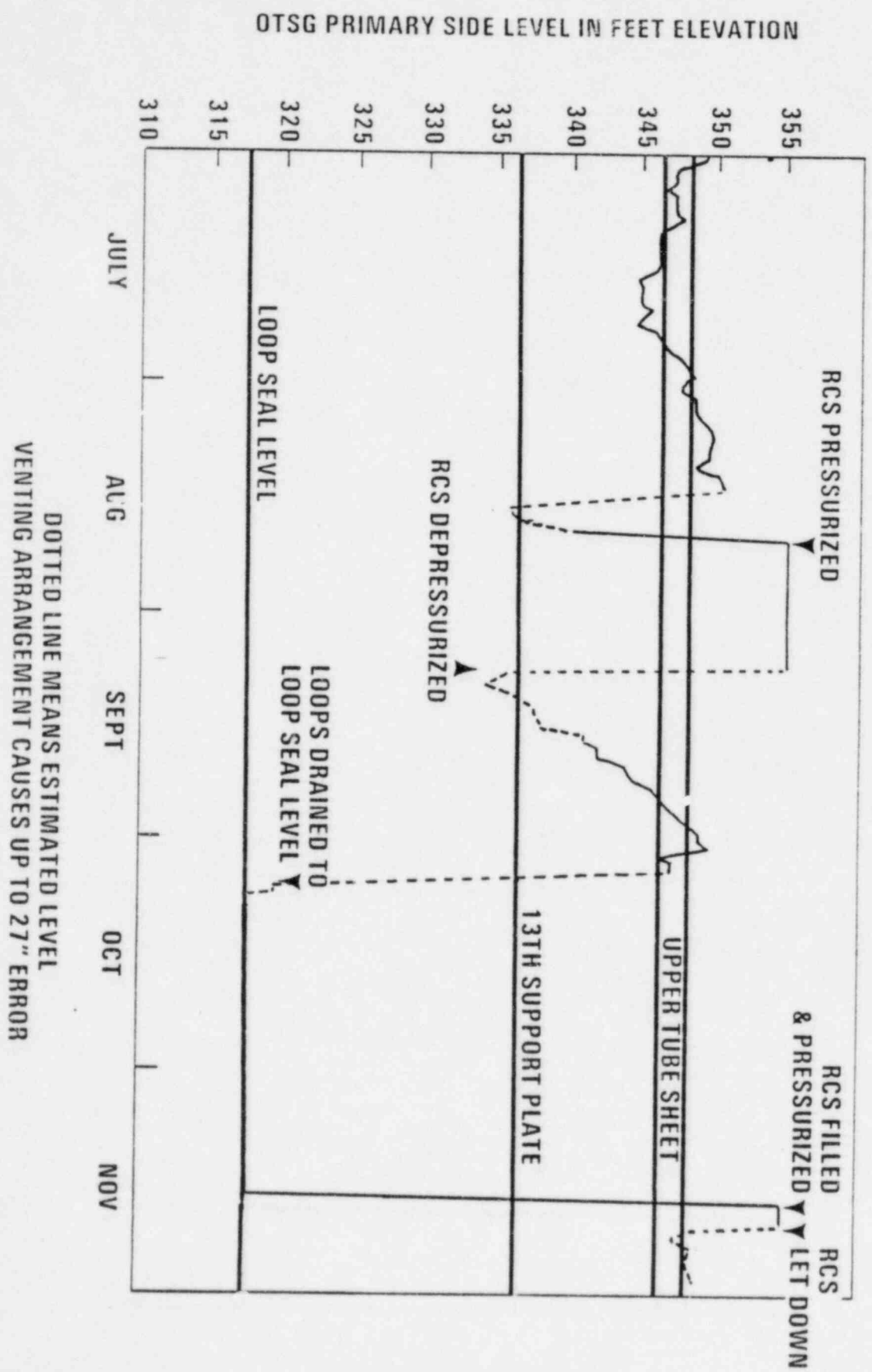| ACTIVITY	RESPONSIBLE INDIVIDUAL	GPUN ORGANIZATION
Group Leader	R. Long	T & E
Met & Cracking Test	S. Giacobbe	Matls. Tech
SG Fabrication History	J. Wildermuth	QA
Chemistry History	K. Frederick	Systems Lab.
SG Operating History	J. Jones	T & E
Chem. and Swipe Samples	M. Campagna/J. Tangen	Proj. Engr./Chem. Engr.
Industry Experience & Research	R. Jones (EPRI)	
Full Time Task Support	J. Paules	TMI-1 STA
	H. Crawford	TMI-1 STA
	J. Tangen	Chem. Engr.
Assigned Task Support	J. Sipp	Chem. Engr.
	R. Demuth	Matls. TF
	H. Shipman	Plant Engr.
	G. Reed	Plant Chem.
	A. Clemons	T & E
	J. Moore	Tech. Functions
Independent Metallurgical Consultant	J. Janiszewski	
Stress Analysis	S. Weems (MPR)	
Metallurgical Failure Analysis	A. Agrawal (Battelle)	

I - 11

TABLE I - 2

<u>B&W FAILURE ANALYSIS TASK GROUP</u>

ACTIVITY	RESPONSIBLE INDIVIDUAL	GPUN ORGANIZATION
Group Leader	J. Olszewski	Mech. Engr.
Met & Cracking Test	G. Clevinger/G. Theus	LRC/ARC
SG Fabrication History	R. Boberg	Mech. Engr.
Chemistry History	M. Bell	Engr.
Chem. and Swipe Samples	M. Bell	Engr.
Full Time Task Support	J. Smith	Mech. Engr.
	R. Carey	Mech. Engr.
	M. Rigdon	LRC
Assigned Task Support	R. Post	Mech. Engr.
	R. Pelger	ARC
	E. Pardue	LRC
	T. Hardt	LRC

OTSG PRIMARY SIDE LEVEL IN FEET ELEVATION

FIGURE I-1

OTSG Level
July 1981 — November 1981

355 — 350 — 345 — 340 — 335 — 330 — 325 — 320 — 315 — 310

JULY   AUG   SEPT   OCT   NOV

RCS PRESSURIZED

RCS DEPRESSURIZED

LOOP SEAL LEVEL

LOOPS DRAINED TO
LOOP SEAL LEVEL

13TH SUPPORT PLATE

UPPER TUBE SHEET

RCS FILLED
& PRESSURIZED

RCS LET DOWN

DOTTED LINE MEANS ESTIMATED LEVEL
VENTING ARRANGEMENT CAUSES UP TO 27" ERROR

II. DESCRIPTION OF OTSG'S AND CRACKING PROBLEM

A. Summary Description of OTSGs

The OTSGs are vertical straight tube and shell, once through heat exchangers (See Figure II-1) with shell side boiling that produces super-heated steam at constant pressure at the turbine throttle (about 925 psia and 570 to 590° F) over the power range. Primary coolant from the reactor enters the steam generator through a nozzle at the top, flows downward through more than 15,000 Alloy 600 (Ni, Cr, and Fe) tubes, is collected in the bottom head, and exits through two outlet nozzles. On the secondary side, the subcooled feedwater is sprayed downward into a steamfilled annulus between the shell and tube-bundle shroud where it is heated to saturation temperature by direct condensation of steam on the water droplets. The saturated feedwater then enters the tube bundle at the lower tubesheet where nucleate boiling begins. After reaching 100% quality, the steam becomes superheated, leaves the tube bundle above the 15th tube support plate (TSP), flows downward through a steam annulus, and exits through two steam outlet nozzles.

Tube support plates maintain the tubes in a uniform pattern along their length. A unique feature of the design is the broached tube support plate concept (Figure II - 2). These tube support plates are fabricated from 1 1/2 inches thick carbon steel, drilled, and broached at three points spaced 120° apart. The broached design effectively eliminates stagnant areas where solids can concentrate by creating large openings for the flow of water and steam.

Another feature in the OTSGs is an untubed inspection lane (Figure II-3). This lane is formed by omission of a row of tubes halfway across the tube bundle to facilitate inspection of the tube bundle and possible chemical cleaning at some time later in the operating life of the equipment.

The attached exhibits provide additional general OTSG data:

> Table II - 1 - General OTSG Data
> Figure II - 4 - OTSG Longitudinal Section Elevations (Typ.)
> Figure II - 5 - TMI-1 OTSG Upper Tube Sheet Detail (Typ.)
> Figure II - 6 - OTSG MFW, AFW, and Steam Penetrations

B. OTSG Heat Transfer

The characteristics of the four heat transfer regions that exist in the OTSG as feedwater is converted to superheated steam are described further:

1. Feedwater Heating.

   Feedwater is heated to saturation temperature by direct contact heat exchange. The feedwater entering the unit is sprayed into the downcomer annulus formed by the

shell and the cylindrical baffle around the tube bundle (see Figure II-4). Steam is drawn by aspiration into the downcomer and heats the feedwater to saturation temperature. The saturated water level in the downcomer provides a static head to balance the static head in the nucleate boiling section, and the required head to overcome pressure drop in the circuit formed by the downcomer, the boiling sections and the bypass steam flow to the feedwater heating region. The downcomer water level varies with steam flow from 15 to 100% load. A constant minimum level is held below 15% load.

2. Nucleate Boiling.

The saturated water enters the tube bundle just above the lower tubesheet and the steam-water mixture flows upward on the outside of the tubes countercurrent to the reactor coolant flow. The vapor content of the mixture increases almost uniformly until DNB is reached, and then film boiling and super-heating occurs.

3. Film Boiling.

Dry saturated steam is produced in the film boiling region of the tube bundle.

4. Superheated Steam.

Saturated steam is raised to final temperature in the super-heater region. The amount of surface available for superheat varies inversely with load. As load decreases the superheat section gains surface from the nucleate and film boiling regions. Mass inventory in the steam generator increases with load as the length of the heat transfer regions vary. Changes in temperature, pressure and load conditions cause an adjustment in the length of the individual heat transfer regions and result in a change in the inventory requirements. If the inventory is greater than that required, the pressure increases. Inventory is controlled automatically as a function of load by the feed-water controls in the integrated control system.

Primary and secondary side OTSG operating temperatures vary over the power range. Typical operating temperatures are presented in Figure II - 7. In addition, Figure II - 8 is attached to illustrate primary fluid, secondary fluid, and tube wall tem-peratures over the length of the OTSG at 100% power.

C. Description of Intergranular Attack

1. Basic Phenomenon

The failure mechanism responsible for the cracking of the TMI Unit 1 steam generator tubing is stress assisted intergranular

attack. This phenomenon preferentially attacks the material grain boundaries by electrochemical dissolution, then under the influence of stress, forms a continuous crack network perpendicular to the applied stress direction. In the case of the TMI-1 steam generator tubes the cracks were circumferential in orientation and the corrodant responsible for the attack is believed to be a reduced sulfur species.

2. Results of Eddy-Current Examinations

In-situ eddy-current results exhibits tube wall defect indications at varied rates distributed both axially and radially in both OTSG 'A' and 'B' tube bundles. The majority of the defect indications are in the upper tubesheet (UTS) region and particularly confined in the tube roll transition zone. Ninety-five (95) percent of all tubes with defect indications are contained in the top seven (7) inches of UTS with less than 200 tubes containing defect indications below the UTS (80 percent of those defects are above the top support plate). Radial distribution of tubes with defect indications in 'A' OTSG shows a high percentage in the UTS periphery with the defect rate decreasing rapidly as you move toward the center of the bundle. In the 'B' OTSG, however, half of the UTS exhibits an approximate 20 percent defect rate with defect rates to 90 percent in a broader peripheral area of the other half. Reference 9 documents defect rates in detail.

TABLE II - 1

GENERAL OTSG DATA

Height:

Bottom of Support Skirt to Top of Inlet Nozzle   73 ft., 2 1/2 in.

Weights:

Shipping	:70 tons
Flooded	7 0 tons
Operating (15% load)	62ᵢ tons
Operating (100% load)	637 tons

Pressures:	Design	Full Load Operating	Hydrotest
Primary	2500 psig	2200 psia	3125 psig
Steam Outlet	1050 psig	925 psia	1312.5 psig
Feedwater	1100 psig	---	---
Primary Drop		33 psi	

Temperatures (°F)	Design	Full Load Operating	Hydrotest (min) (Shell Temp.)
Primary	650	602 Inlet	100
Secondary	600	595	100
Feedwater	600	470	

Operating Limits and Precautions

Minimum Pressurization Temperature	100F
Maximum Heatup/Cooldown Rate	100 F/hr
Minimum Annulus Water Temperature	10 F below saturation hydrotest pressures

Operating Conditions (Full Load)

Heat Transfer	4.35×10^9 BTU/hr
Primary Fluid Flow	68.94×10^6 lb/hr
Stem Flow	5.30×10^6 lb/hr

Heat Transfer Tubes

Number	15,531
Material	Inconel alloy 600
Size	0.625 O.D., 0.034 minimum wall, 56 ft., 2-3/8 in. long, with 52 ft. 1-3/8 in. heating length

Total Heating Area   132,436 ft.^{2}

FIGURE II-1

Once-Through Steam Generator

- Reactor Coolant Inlet
- Manway
- Auxiliary Feedwater Nozzle
- 15th
- 14th
- 13th
- Steam Annulus
- Steam Outlet
- 10th
- 9th
- Feedwater Inlet
- Feedwater Heating Annulus
- Tube Support Plate
- Handhole
- Reactor Coolant Outlet
- Manway
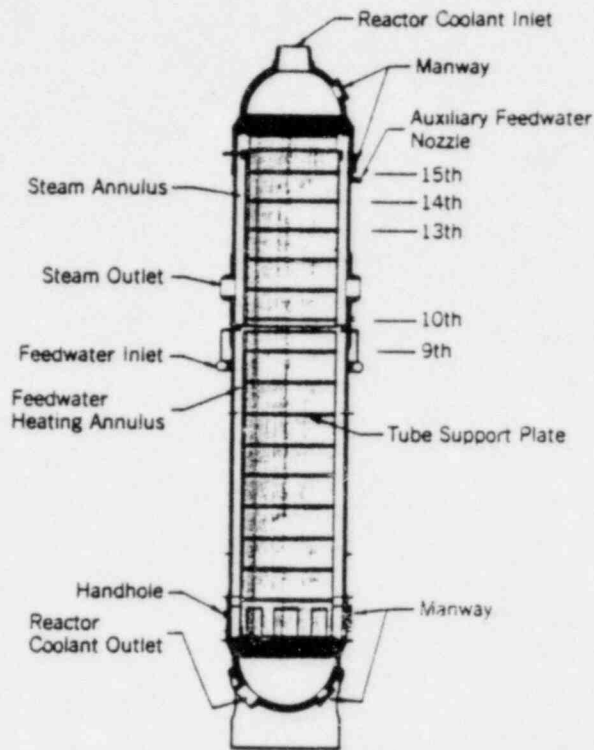
FIGURE II - 2

OTSG Broached Tube Support Plate

Tube pitch .875" - .010"

Minimum outside tube radius .3125 inches

Minimum drill radius .320 inches
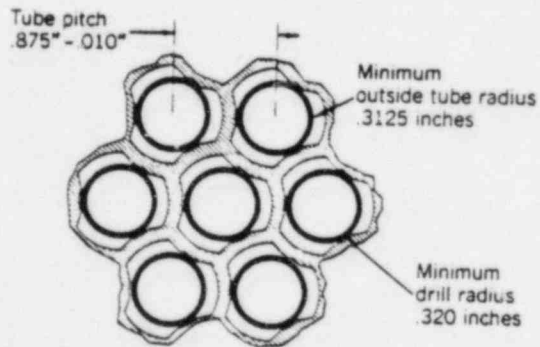
Note: Plates fabricated from 1½-inch thick plate.

FIGURE II - 3

Tube Bundle Cross Section Showing Lane

W

Z

X

Lane

Y

○ Tube

FIGURE II - 4

OTSG Longitudinal Section
Elevations (Typ.)

PRIMARY SIDE
(INSIDE TUBES)

UPPER
TUBESHEET (UTS)

AUXILIARY
FEEDWATER
NOZZLES
(AFW)

STEAM OUTLET

MAIN FEEDWATER
NOZZLES (MFW)

SECONDARY SIDE
(EXTERNAL TO TUBES)

TUBE
SUPPORT
PLATES

LOWER
SECONDARY
HANDHOLE

LOWER
SECONDARY MANWAY

LOWER
TUBESHEET (LTS)

REACTOR BLDG. FLOOR

ELEVATION
FEET

346'6"
342'8"
339'9"
336'5"
333'8"
330'6"
327'4"
324'4"
321'1"
317'9"
314'6"
311'8"
308'5"
305'1"
301'10"
298'8"
294'5"
281'0"

15TH
14TH
13TH
12TH
11TH
10TH
9TH
8TH
7TH
6TH
5TH
4TH
3RD
2ND
1ST

FIGURE II-5

TMI-L OTSG Upper Tubesheet Detail (Typ)

.051" MIN. → ← .635" REF.

← .051" MIN.

.187 →

.035 MIN.

5/16" CLADDING   1" MIN. EXPANSION

24" - 5/16"

.875" ± .010"

.240 TYP.

.7578 (Ref

.875"   .875"

TYP. TUBE PATTERN

.625" TUBE O.D. X .034"
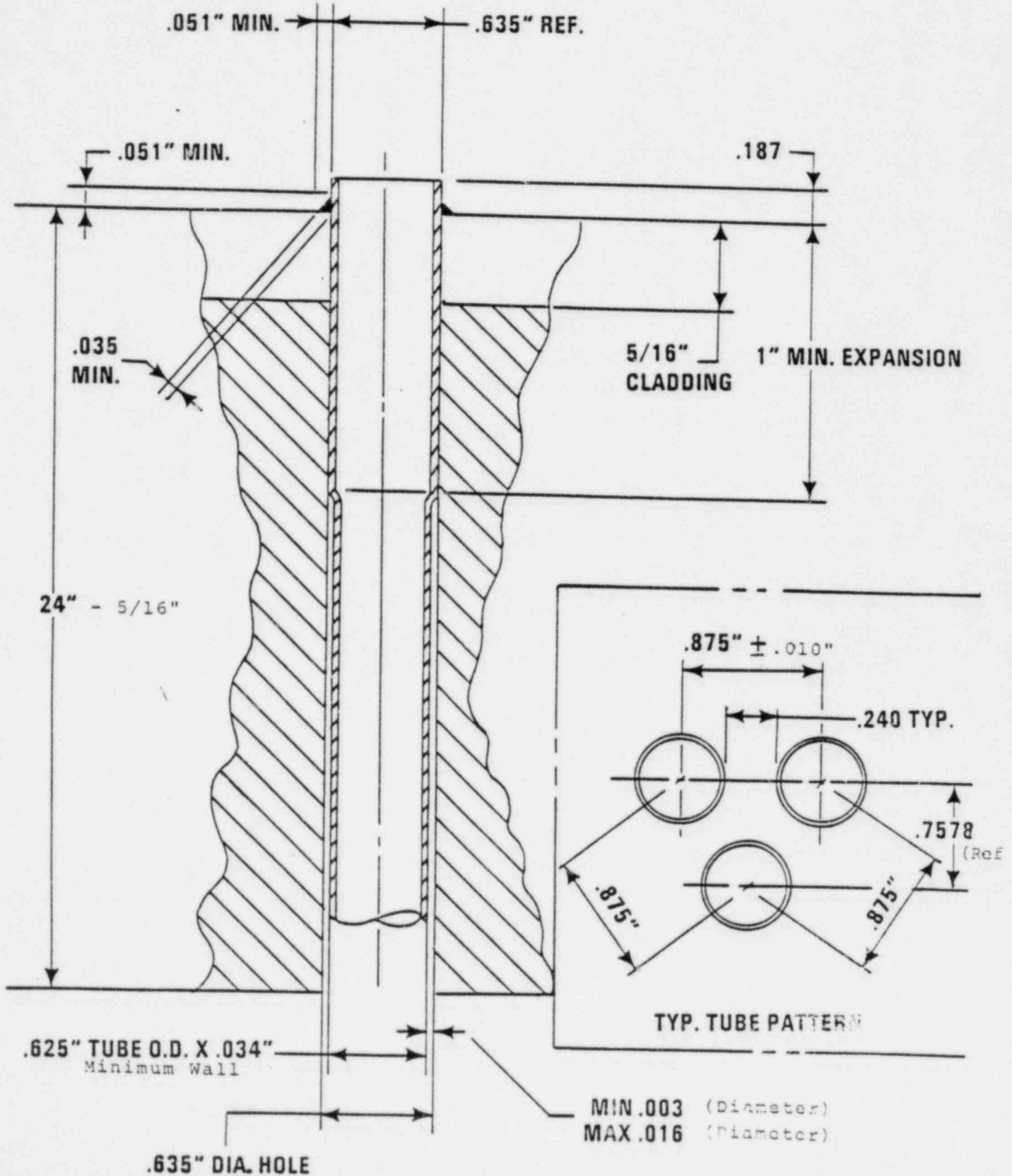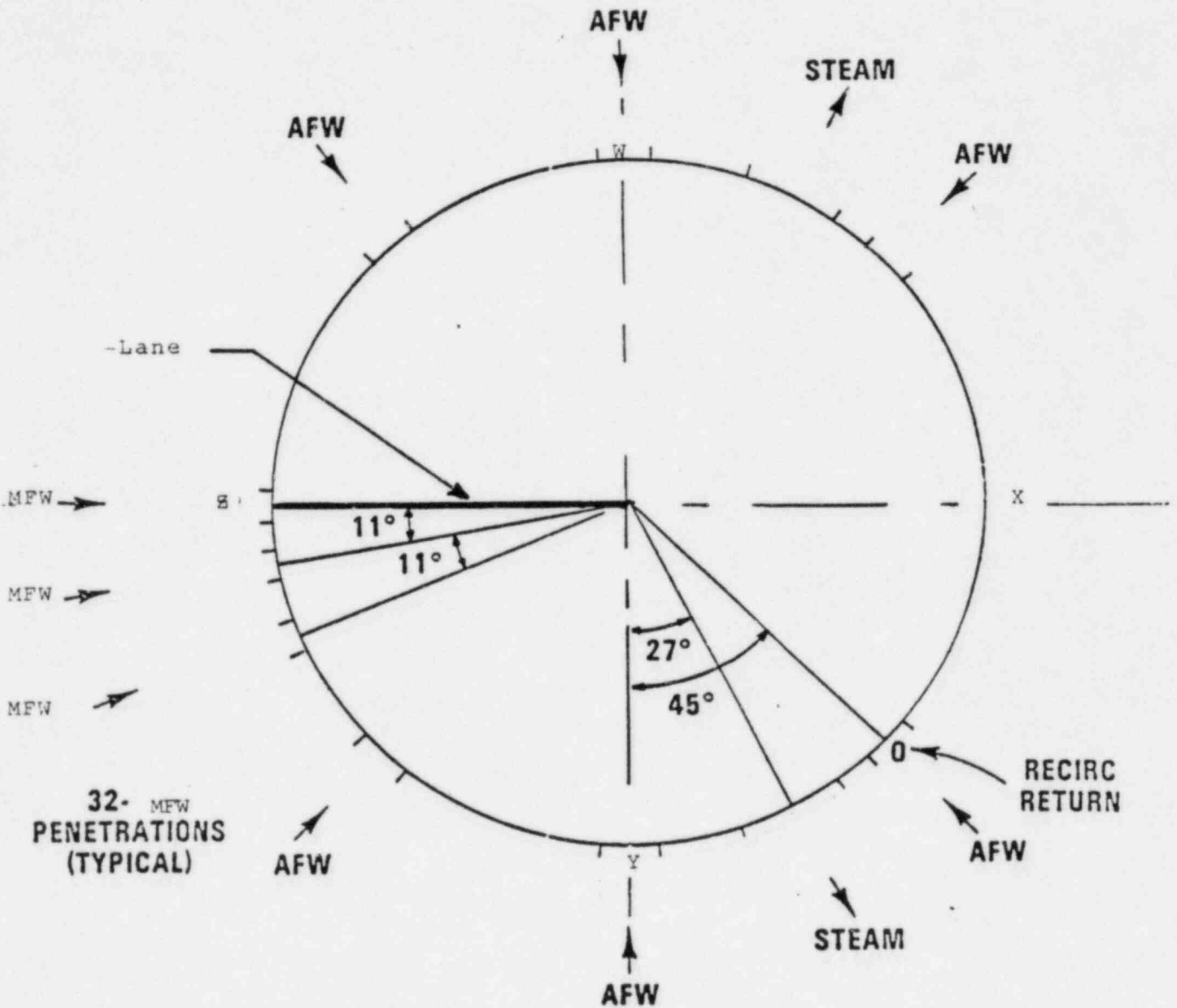Minimum Wall

MIN .003 (Diameter)
MAX .016 (Diameter)

.635" DIA. HOLE

FIGURE II - 6
OTSG, MFW, AFW, and Steam Penetrations

Steam: 2-24" Steam Outlet

AFW: 6-2 Inlets, (Originally 7.Z-Axis plugged in 1980.) Located ∼ 36" below lower
edge of UTS

MFW: 32-3" Inlets, spaced ∼ 11° around OTSG.

Recirc Return: Returns through UTS vent and level sensing connection.
∼ 14" from lower edge of UTS. 1" connection.

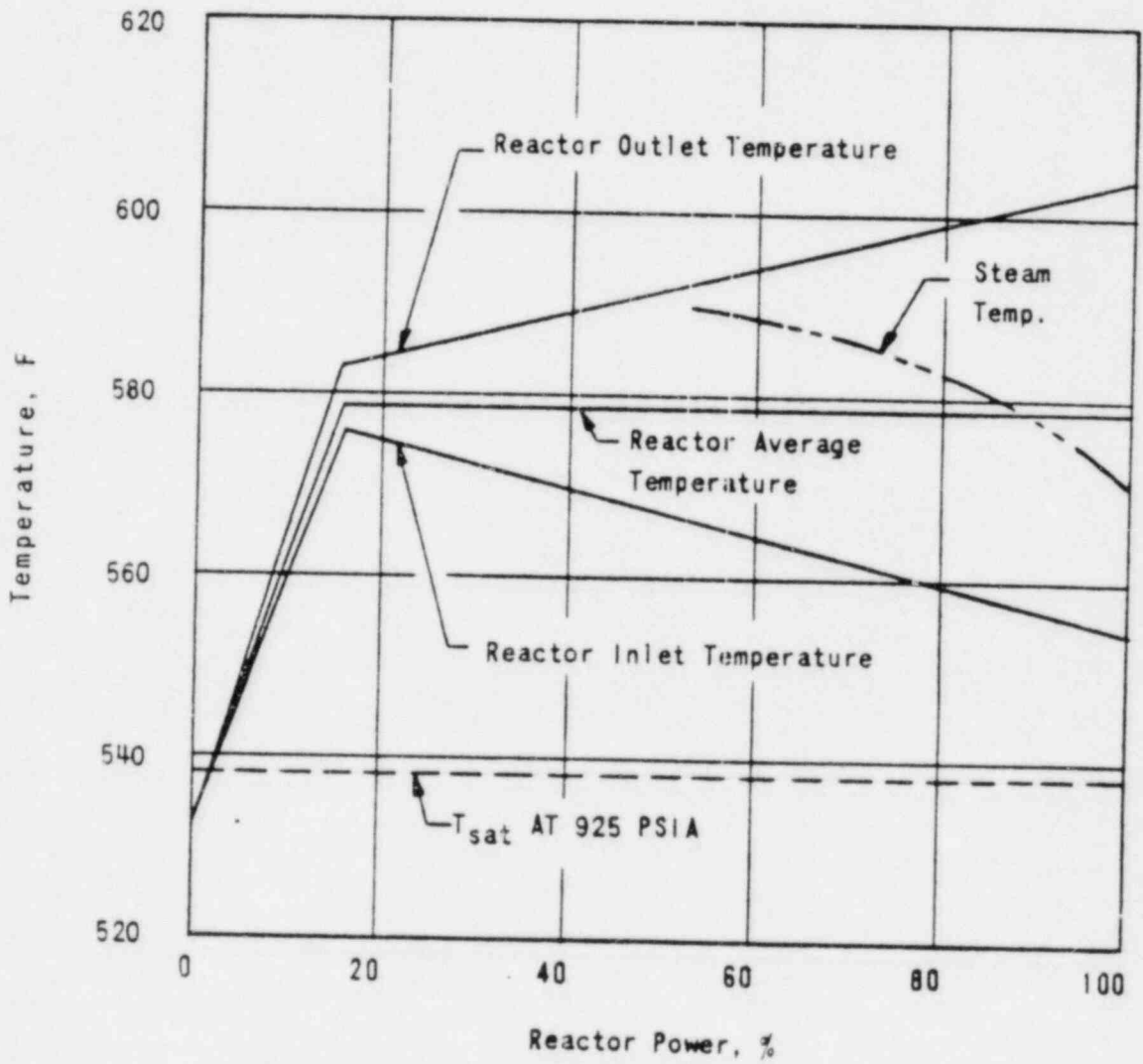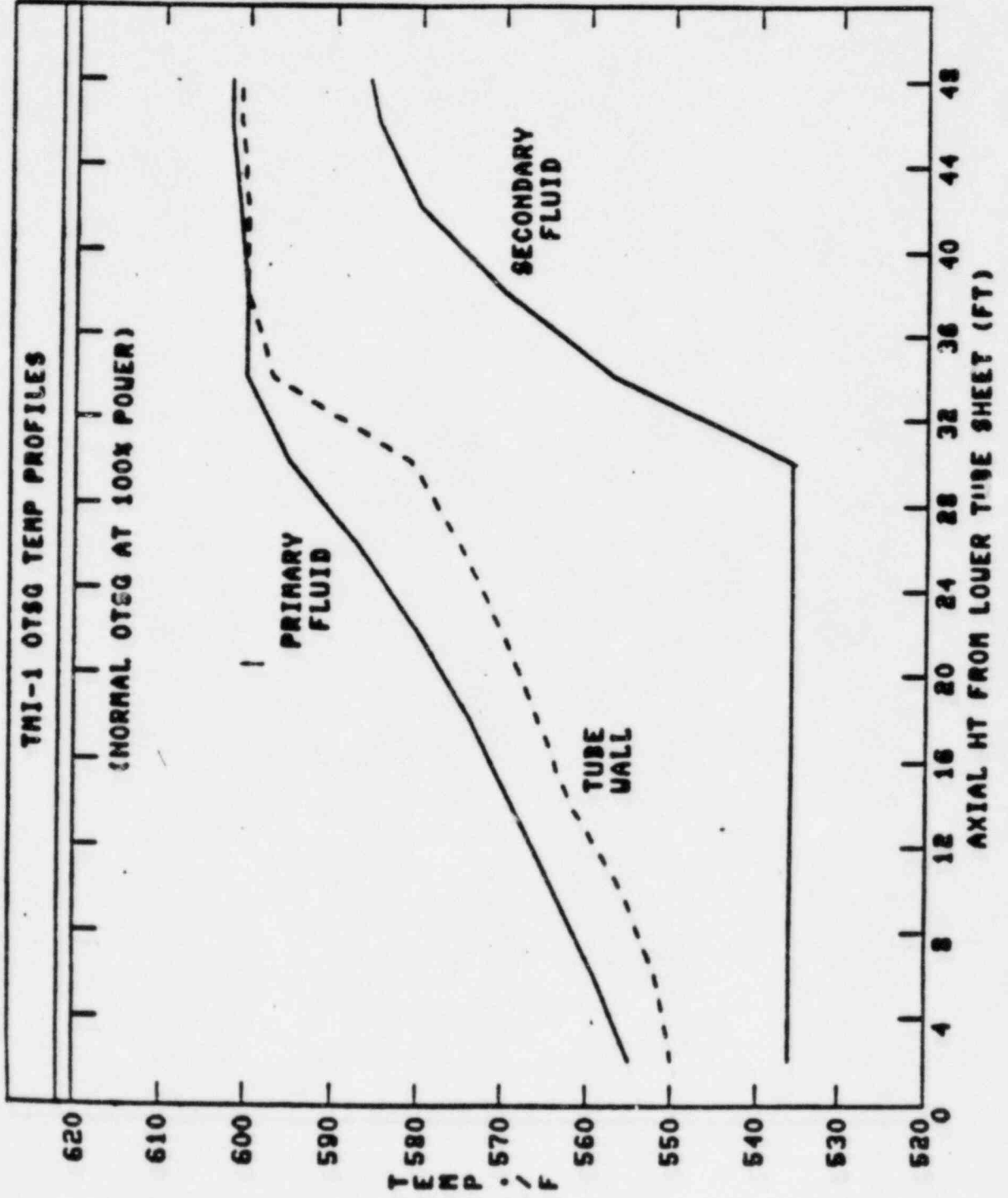FIGURE II - 7

OTSG Primary and Seconday Temperatures Versus Load

FIGURE II - 8

TMI-1 OTSG TEMP PROFILES

(NORMAL OTSG AT 100% POWER)

PRIMARY FLUID

SECONDARY FLUID

TUBE WALL

TEMP °F

620 610 600 590 580 570 560 550 540 530 520

AXIAL HT FROM LOWER TUBE SHEET (FT)

0 4 8 12 16 20 24 28 32 36 40 44 48

III-1

III. OTSG OPERATING HISTORY

A. Purpose and Key Points

1. Statement of Purpose

The failure of the OTSG tubes by intergranular stress assisted cracking leads us to examine the environment to which the tubes have been subjected. The purpose of this analysis of the operating history is to provide information on those environmental parameters which might reasonably have had some impact on the tube failures. Included as elements of the operating history are those incidents in which the introduction of chemical contaminants into the reactor coolant system is considered likely.

2. Summary of Key Points

a. The water surface in the primary side of the OTSG's during the layup period since Feburary 1979 has been in the upper tube sheet for a minimum of 31 days and a maximum of 243 days. The large uncertainty is due to the lack of good data on reactor coolant drain tank level.

b. It is probable that oil was introduced into the reactor coolant system in early March 1979.

c. It is probable that sulfuric acid was introduced into the reactor coolant system in mid-October 1979.

d. It is probable that sodium thiosulfate was introduced into the reactor coolant system in July 1980, May 1981 and early September 1981.

B. Methods

In collecting the operational data, a review was made of operator logs, shift foremans' logs, and automated printouts. In addition, interviews were conducted with plant operators and supervisory personnel. Two TMI-1 shift technical advisors were assigned to this task full time.

C. Results

1. Pressure, Temperature and Level Plot

The environmental parameters of pressure, temperature, and level in the primary side of the OTSG are plotted over the period February 1979 to November 1981. Reference 1. contains these plots. There is at times an uncertainty of about 55 inches in the OTSG primary side level due to the venting arrangement of the reactor coolant hot legs and the pressurizers. The graphs show pressurizer level and include the uncertainty in OTSG level as a reference line below the level of te OTSG upper tube sheet. Thus, when the plot of pressurizer level is above the reference line, OTSG level may lie in the upper tube sheet. Figure III-1 shows schematically the venting arrangement which gives rise to the uncertainty. The difference in level between the pressurizer and the OTSG is the level of water in the reactor coolant drain tank. This tank level is not always recorded. When the drain tank level was recorded, both pressurizer and OTSG level were plotted. The OTSG level is always the higher level. Figure I-1 summarizes OTSG level behavior for the period July - November 1981.

2. Contamination Incidents

Among the significant events considered to have an impact on the OTSG environment were incidents of possible chemical contamination of the Reactor Coolant System (RCS). Three such incidents have been identified. The possibility that resin breakdown contributed chemical contaminants was considered and found not to be likely. Section IV. B. 7 of this report refers.

a. Sodium Thiosulfate

The possibility of contamination of the RCS by sodium thiosulfate was investigated and found to be probable. This investigation is reported in Reference 1. A summary of the results of that investigation is provided here.

It has been determined that liquid from the sodium thiosulfate tank reached the suction piping of the Reactor Building (RB) spray pumps by two possible flow paths. The first is leakage through the BS-V-4A/4B valves. The second is past the BS-V-4A/4B valves when cycled during the valve surveillance section of S.P. 1300-3A. Chemistry results of samples taken in the RB spray suction and discharge piping in January 1982 show high concentrations of sulfates (14 ppm). It is probable that small quantities of sodium thiosulfate reached the RB spray piping throughout plant life. Prior to the long lay up following the TMI-2 accident, frequent cycling of the RB spray pumps interspersed with Borated Water Storage Tank (BWST) cleanup periods prevented dangerous accumulation of the chemical.

When the RB spray pump surveillance S.P. 1300-3A is performed, each spray pump is placed in the recirculation mode taking suction from the BWST and discharging back into the BWST. This would pump sodium thiosulfate in the RB spray piping into the BWST. This method was used on 6/25/81, 8/30/81 and 9/3/81 for a total of 12.2 hours in the time period since the last refueling. Analysis of the contents of the BWST in January 1982 showed .1 ppm of sulfates. However, the BWST was placed on cleanup through a precoat filter between the last surveillance of the RB spray pumps and the time the sample was taken. This leads to the potential of much higher sulfur contents in the BWST prior to cleanup, possibly as high as 850 ppb.

Sodium thiosulfate in the BWST could be injected into the RCS by using the BWST for normal RCS makeup, by performing the refueling interval surveillances S.P. 1303-11.54, S.P. 1303-11.8, or by leakage. In May of 1981 the BWST was used to add approximately 2000 gallons of water to the RCS. This was prior to the time that the RB spray pumps were run for the surveillance. During September of 1981, near the end of hot functional testing periods and after the RB spray pump surveillance was run, water was injected into the RCS from the BWST while performing T.P. 665/1 and S.P. 1303-11.8 High Pressure Injection (HPI) and S.P. 1301-11.54 Low Pressure Injection (LPI) functional testing. These tests would have injected sodium thiosulfate into the RCS at various temperatures. The last flow path from the BWST to the RCS is leakage past DH-V-5A/5B. These valves have had a past history of leakage. At least twice they have been repaired to try to obtain a tight seat, and leakage through these valves was observed in the period of interest (during the integrated leak rate test). Pressurizer level increased from 208" to 376" between 9/10/81 and 9/27/81 due to this leakage.

Chemistry results have been reviewed which indicate unexplained increases in RCS conductivity and pH between 7/18/80 and 7/25/80 and again between 5/11/81 and 5/18/81. These time frames coincide with the addition of water from the BWST to the RCS. The operational history does not support the proposition that the BWST was contaminated by sodium thiosulfate prior to those additions; or that the piping involved in the water transfer was contaminated. The possibility that unrecorded plant operations occurred which cross contaminated the RCS from the RB spray system can not be discounted, given the limited information in plant logs.

To preclude future problems with sodium thiosulfate contamination and since the system is no longer required for its originally intended purpose, the sodium thiosulfate tank and associated piping has been drained and flushed.

b. Sulfuric Acid

The possibility of contamination of the RCS by sulfuric acid was
investigated and found to be probable. This investigation is
reported in Reference 1. The results are summarized here.

On 9 October 1979, 3000 milliliters of sulfuric acid (98%) were
added to approximately 37 to 49 gallons of water in the lithium
hydroxide mix tank (CA-T3). This solution was pumped into the
makeup system using the lithium hydroxide pump (CA-P2). The
tank was filled again with approximately 25 to 37 gallons of
reclaimed water which was subsequently pumped into the makeup
system. (The acid was to have been added to the neutralizer mix
tank (WDL-T8) in the liquid waste disposal system via the
caustic mix tank (CA-T2). The inadvertent addition resulted
from using the lithium hydroxide mix tank instead of the caustic
mix tank.)

The error was not recognized until October 13, 1979. Samples
were taken at several locations in the makeup system on October
14, 1979, in an attempt to determine the location of the acid
and establish boundaries for a system flush. A special
operating procedure was prepared to flush the makeup system.
The lines were flushed with reclaimed water until the pH was
greater than 5. A second flush with borated water was performed
to flush the lines to the RCS. The flushes were performed from
October 14 through October 25, 1979.

In order to verify that the acid did not reach the RCS, a sample
was taken on 1 November 1979 and analyzed by B&W. The analysis
indicated less than 0.66 ppm sulfur (less than minimum
detectable with the analysis used).

Although preventive actions were taken, it appears that some of
the acid may have reached the RCS. The initial sample taken at
MU-V-207, which ties in just upstream of MU-V-18, indicated a pH
of 1. This indicates flow through this portion of the system.
The position of MU-V-18 at the time of the acid addition is
uncertain. The last valve lineup that was signed off on 9/7/79
indicates that MU-V-18 should have been open, however, it was
not signed off; a "CR" was placed next to the position in-
dicating control room control of valve position. The shift
foreman's log indicates that the positions of MU-V-78 and
MU-V-47 were changed in order to add water from "B" reactor
coolant bleed tank to raise pressurizer level on 9/7/79. This
operation would have required MU-V-18 to have been opened. No
guidance is given to the operator as to what to do with MU-V-18
after the operation is complete, he may shut it or leave it

open. MU-V-78 and MU-V-79 were left in their fill lineup posi-
tions which prevented the acid from going directly to the makeup
tank. The initial flush procedure does not require operation of
MU-V-18 for the first flush path. This flush path required the
flush water to flow through MU-V-18, implying that MU-V-18 was
open. If the valve was open, a continuous flow path to the RCS
existed. If the valve was shut, a restricted flow path existed
due to leakage past MU-V-18.

Samples for pH were also taken at MU-V-143B and MU-V-159B which
are downstream of MU-V-18. MU-V-143B had a pH=5. MU-V-159B had
a pH=6. If check valves MU-V-107B and MU-V-94 did not leak,
then the flow of water for these samples would have been from
the makeup system. Since the water had a pH=1 at MU-V-207, this
flow would draw the low pH water closer to the RCS and possibly
past MU-V-143B when sampling MU-V-159B. If the check valves did
leak, the low pH water may or may not have been drawn into this
line.

The first flush path of the initial flush procedure supplied
reclaimed water at MU-V-143B and drained through MU-V-207. If
low pH water was in the line between MU-V-143B and MU-V-159B,
the pressure of the reclaimed water would have been sufficient
to drive this water into the RCS.

pH samples taken at a drain on each of the makeup pumps also
indicated pH=1, indicating flow through this portion of the
system. Since flow from the lithium hydroxide pump is one-sixth
of a gallon per minute, there is little driving force to seat
check valves in the system. The acid would have had to have
passed through MU-P1A and MU-P1B discharge lines to the pumps.
Leakage past the bearing seals would account for some flow and
MU-V-12 possibly being open may have accounted for additional
flow. MU-V-76A, MU-V-76B, MU-V-69A and MU-V-69B are normally
locked closed and there is no evidence of changes in these valve
positions. Therefore, for acid to reach MU-P1C would require
flow through the pumps' recirculation lines and/or through
leaking valves. Some flow of the acid through the makeup pumps
may also have occurred during the flushes on other parts of the
system.

Review of the RCS chemistry for this period indicates a signifi-
cant change in pH and conductivity with essentially no change in
boron concentration. Calculations were performed to estimate
the volume of acid necessary to cause the change in pH. The
volume of acid was relatively small, being approximately 0.4
liters of the concentrated acid.

Calculations predict a sulfur concentration that should have been detectable by the B&W analysis that was performed. However, that sample was obtained on 1 November 1979 which was after approximately 15,000 gallons of water was added to the Reactor Coolant System. This addition of water would have reduced the sulfur concentration to a value below the minimum detectable concentration.

Assuming that sulfuric acid in the amount indicated did find its way into the RCS, it is unlikely that the attack on the OTSG tubes resulted directly. The sulfur in sulfuric acid is in the form of sulfate which is not an aggressive species at ambient temperature in the reactor coolant environment. There is a possibility that it could be aggressive at elevated temperatures. Also, in the presence of sodium thiosulfate, a reduction in pH could activate the corrosion mechanism.

c.   Oil

The possibility of contamination of the RCS by oil has been investigated. Findings indicate that such contamination is likely to have occurred in March 1979.

Probable overfilling of the miscellaneous waste storage tank is a likely mechanism by which oil might be introduced into a reactor coolant bleed tank and subsequently into the RCS. Another mechanism considered was the possible contamination of the nitrogen cover gas by oil. This has been found not to be the case. The nitrogen supplied to TMI-1 is not produced in such a way as to allow oil contamination.

If in fact oil were introduced into the RCS in the amounts possible, it is unlikely that it would by itself result in the observed attack on the tubes. The quantity of sulfur available is too low. Reference 1. details these findings.

3. Timing of the Tube Failures

The time of the OTSG tube failures may be bracketed based on operationa considerations. During hot functional testing on 9/4/81 at 0637, the leak rate of the RCS at full pressure was measured and found to be within specifications at 0.5 gallons per minute. On 11/21/81 with the RCS at about 40 PSI pressure leakage through the OTSG tubes were observed.

One other incident which might bear on the timing of the tube failures was an abnormal depletion of hydrazine on the secondary side of the OTSG's. In the A OTSG between 9/9/81 and 9/16/81 hydrazine decreased from 92 ppm to 16 ppm. In the B OTSG between 9/17/81 and 9/23/81 hydrazine decreased from 68.75 ppm to 0.012 ppm. These decreases were attributed to work on the OTSG AFW piping which was going on at the time.

A possible scenario is that failed OTSG tubes allowed negative pressure on the primary side containment to draw air into the secondary side despite the normal nitrogen purge.

4. Consideration of Asymmetric Failure Patterns

The radial distribution of the failures in each OTSG has some similarity. Consideration was given to the fact that the distribution of Auxiliary Feedwater nozzles around the periphery of the OTSG roughly corresponds to the distribution of the failures. The Auxiliary Feedwater nozzles at TMI-1 were used only once. During the loss of power testing in 1974 flow was initiated through this path when the primary temperature was about 550°F. The nozzles have not been required to be used since. It is unlikely that the location of these nozzles had any operational effect on the tubes.

The radial distribution of the failures also displays some dis-similarities. The failures in the B OTSG occurred predominantly in the side opposite the recirculation return nozzle on the secondary side. Consideration was given to the possibility that recirculation of the secondary side may have cooled the tubes near the return line causing condensation and dilution of the agressive environment on the primary side. The A OTSG however was recirculated first following the cooldown from Hot Testing. Additionally, the recirculation flow is not cooled so it does not appear likely that condensation on the primary side would result. The failures in the A OTSG occurred predominantly in the periphery where the tensile stress is higher. In the absence of any clear difference in the material and environment between the A and B OTSG and in the presence of the stress dependence in the A OTSG, it may be inferred that distribution of failures in the B OTSG is stress related.

The fabrication history of the B OTSG does not explain the apparent asymetry in tensile stress in the tubes. One possibility is that the whole steam generator is slightly bowed. Another is that the upper and lower tube sheets are not precisely parallel. In an attempt to confirm asymetry of tube tensile stress, a study is being conducted by Babcock and Wilcox to determine the feasibility of measuring the relative tensile stress in the tubes by measuring the tube's fundamental frequency of transverse vibration.

D. Conclusions

Consideration of the operational history supports the hypothesis that the attack on the OTSG tubes was promoted by sulfur introduced into the RCS as sodium thiosulfate. The probable earlier introduction of oil could not have produced the levels of sulfur contamination observed. The sulfuric acid introduced sulfur in its fully oxidized state which does not promote intergranular stress cracking at ambient temperature in the reactor coolant environment. Clean up was conducted prior to heat up.

Figure III-1
R.C. System Drain Arrangement
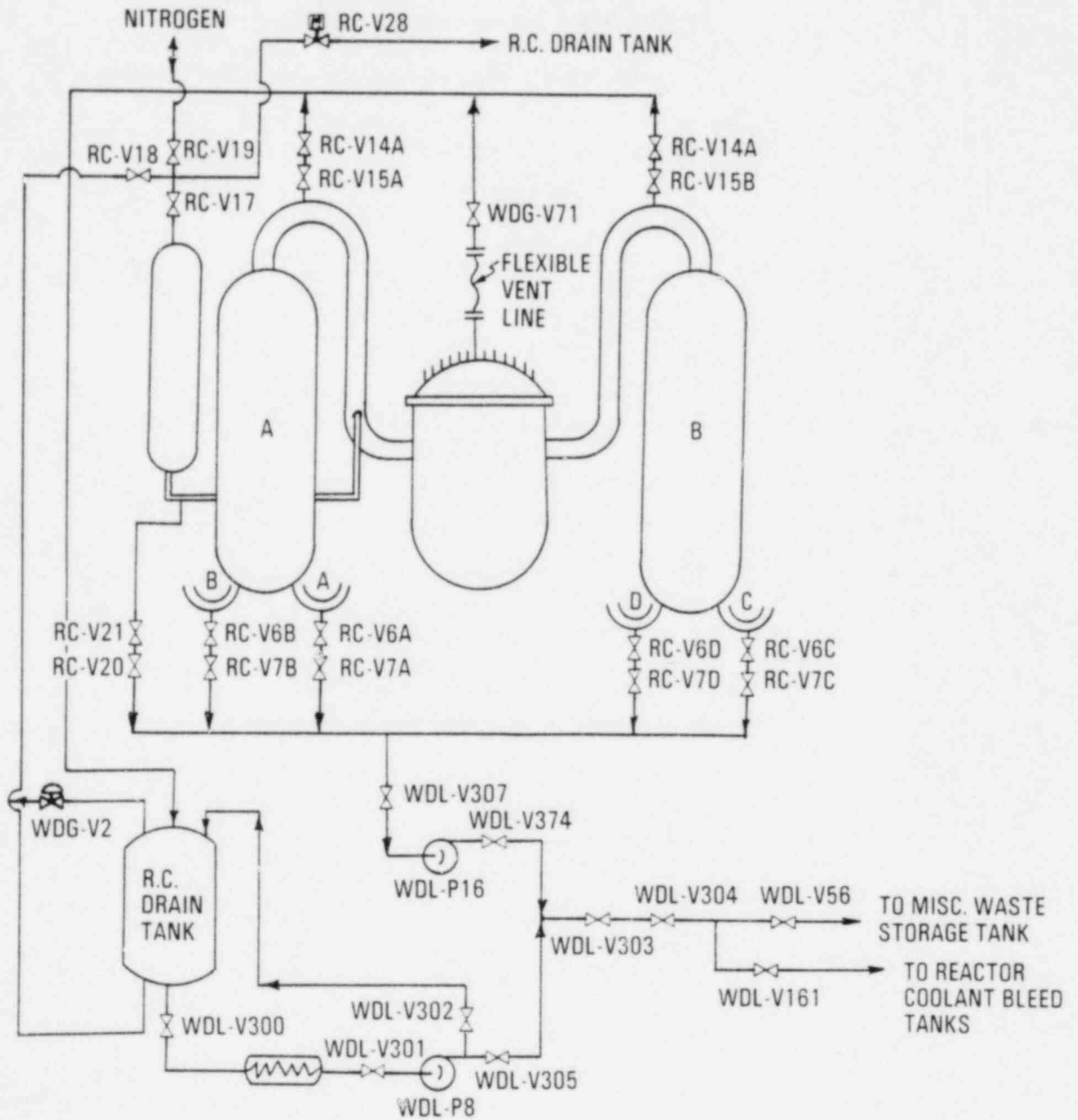
IV. OTSG CHEMISTRY

A. Introduction

Investigation into the chemistry history surrounding the failure of OTSG tubes concentrated upon reactor coolant chemistry in the period between the cooldown of the system in early April 1979, and identification of primary to secondary leakage in November 1981. The efforts were further focused upon parameters and situations which might provide indications of introduction of sulfur or sulfur containing substances into the system. Justification of this direction for intial efforts was based upon initial results from the metallurgical examinations. The first influencing factor was that the failures were initiated from the ID of the tubes. The second factor was that sulfur was identified as a major contaminant present on fracture surfaces. Although lower levels of chlorine were also identified, Inconels are virtually immune to chloride ion stress corrosion cracking.

B. Methods and Results

1. Comparison to Specifications

Initial review involved a simple comparison of historical data with specifications. In general, compliance with the specifications was good. During the entire period, departure from specification was noted only in the chloride parameter with the highest recorded value being 0.5 ppm which was noted on 6/18/79. Values of 0.01 ppm and 0.06 ppm were recorded on 6/15/79 and 6/22/79 respectively. Since no treatment was undertaken during this period, it appears that a contaminated sample or analytical interference was responsible. Several of the other chloride values in the range of 0.1 ppm to 0.5 ppm were surrounded by similar conditions. In any event, industry experience has demonstrated that these levels of chlorides, even if actually present, would not produce chloride stress corrosion cracking when present for only a few days at ambient temperatures.

2. Historical Sulfur Measurements

It became apparent during the review of the historical data that no direct measurements of sulfur or sulfur compounds in the reactor coolant system were available on a regular basis. Some measurements were performed on samples from various points within the spent fuel and rad waste systems which included two samples from the decay heat system and one from the makeup system, in support of the investigation of cracking in spent fuel cooling system piping in late 1979. In addition, a few determinations were made in conjunction with the sulfuric acid induction incident. All of these measurements appear to have been performed by a gravimetric technique with no preconcentration step and, as such, results below 1 to 2 ppm are questionable.

3. Indirect Indications of Sulfur Contamination

Efforts turned to other parameters which might provide indirect
evidence of introduction of ionic species which could not be accounted
for by the specific analyses which were performed. Specific con-
ductivity appeared to be the best such indicator. Boric acid and
lithium hydroxide are known major contributors to the system's specific
conductivity and are added intentionally. Other contributors for which
monitoring is conducted are sodium and chlorides. While an exact
prediction of specfic conductivity resulting from a given combination
of these substances requires calculation of the complex chemical
equilibrium which results, a few of the values recorded in the period
were sufficiently high to require contribution from unmeasured ionic
species. Such unexplained increases occurred in October 1979, July
1980, May 1981 and November 1981. The October 1979 increase can be
attributed to the sulfuric acid induction incident and the November
1981 increase to contamination from inleakage of secondary fluid
through cracked OTSG tubes. The increases in July 1980 and May 1981
both involved transfer of water from the BWST to one of the decay heat
systems. In January 1982, significant levels of sulfur were found in
piping which interconnects with this flow path. In addition, the
analyses have indicated that a major portion of this sulfur was in the
form of the thiosulfate ion. Figures IV-1 and IV-2 show some of the
key chemical parameters for these two periods.

4. July 1980 Incident

In Figure IV-1, the pronounced conductivity and pH increases
between 7/18/80 and 7/25/80, while other parameters exhibit little or
no change, are significant. These changes can be explained by the
addition of small quantities of the mixture of sodium thiosulfate,
sodium hydroxide and boric acid which was contained in the sodium
thiosulfate tank. All parameters had returned to normal by 8/8/81.
The reductions in specific conductivity and pH can be attributed to
processing of the decay heat system through a resin coated precoat
filter and mixed bed demineralizer from 8/4/80 to 8/5/80 and through a
resin coated precoat filter from 8/5/80 to 8/11/80. Removal from the
bulk water of virtually all of the intruding ionic species is
indicated.

5. May 1981 Incident

Similar increases were noted between 5/11/81 and 5/18/81 and are
shown in Figure IV-2. This incident was not, however, immediately
followed by a cleanup of the decay heat system and it appears that part
of the intruding ionic species remained in the system for an extended
period. A resin coated precoat filter was employed from 8/9/81 to
8/11/81 and resulting drop in specific conductivity indicates removal
of approximately 60% of the intruding ionic species. A subsequent test
conducted at GPU System Laboratory to determine what levels of con-
tamination by the mixture from the thiosulfate tank would produce a
specific conductivity change of 11 umho in a simulated reactor coolant
solution indicated that 6-7 ppm as sodium thiosulfate would have been

required. This corresponds to 4-5 ppm as thiosulfate ion. Assuming
this intial level, approximately 1-2 ppm as thiosulfate would have
remained in the system until the fill and vent process at the beginning
of HFT.

6. Oil Introduction

An additional incident which has a potential for inducing sub-
stances which contain sulfur into the system occurred a few days before
the TMI-2 accident. Oil or oil-like substances were discovered in
auxiliary systems which have direct communications with the reactor
coolant system. Extensive documentation of this incident is not avail-
able, probably because of the shift in priorities following the acci-
dent. One value of 2.8 ppm as oil and grease was recorded in the BWST
bulk water and a footnote in a chemistry log book indicates the
presence of oil in a sample from a RCBT which also appeared to have a
very high crud content.

a. Crud Measurements

Selected crud values from Reactor Coolant Bleed Tanks A, B, and C
are presented in Table IV-1. It should be noted that values signi-
ficantly greater than the normal _ 0.1 ppm were recorded as late as
9/5/81. The analytical technique employed for crud analysis is a
gravimetric one and the filters are dried at approximately 105°C, a
temperature which would volatilize little, if any, of the hydro-
carbons in oil or grease.

b. Recent Oil and Grease Results

In addition, oil and grease analyses were perfomed cn a number of
samples taken from the decay heat and associated primary systems
during March and April of 1982. The results are presented in Table
IV-2. Significant levels of oil and grease were recorded in RCBT
A, RCBT B, and the BWST. These levels were observed in samples
dipped from the surface and should be regarded only as qualicative
evidence of the presence of oil or organics and not as a quantita-
tive measure of these substances in the bulk liquid.

7. Resins as a Source of Sulfur

Consideration was given to the possiblity that breakdown of plant
demineralizer resins might release sulfur to the RCS. Two concepts
were examined. First, the resins in the demineralizer were con-
sidered. Only the cation form may release sulfur due to radiation
damage and it is very hardy, requiring greater than 10^8 rad to break
down. Thus the resin in the demineralizer did not break down from
known radiation effects. Secondly, consideration was given to the
possibility that resin escaped into the RCS where high temperatures
could have caused breakdown. There is no indication that this oc-
curred. In particular, crud measurements on the RCS did not reflect
the presence of resin or resin fines.

C. Conclusions

The following conclusions may be drawn:

1. Generally, the reactor coolant system remained within specifications for those parameters for which an analysis requirement existed for the period extending from April 1979 through November, 1981.

2. Two incidents of intrusion of ionic substances not accounted for by specific analyses have been identified. Sodium thiosulfate at levels of 4-5 ppm as thiosulfate is considered to be the most likely contaminent.

3. The ionic species from the first contamination incident in July, 1980, were removed from the bulk liquid by demineralization in August, 1980.

4. The ionic species from the second contamination incident in May, 1981, appear to have been only partly removed by processing through a resin water precoat filter in August, 1981. A 1-2 ppm thiosulfate residual could have still been present at the start of fill and vent prior to hot functional testing in September, 1981.

5. Induction of an unidentified organic substance, probably oil or grease, into RCS auxiliary systems occurred in mid-March, 1979. The exact quantity of this substance or its potential role in any failure mechanism has not been established. Reference 1. documents this incident.

D. Chemistry of Sulfur in Water

Since the matallurgical results indicate that sulfur was involved in the attack on the OTSG tubes, a brief discussion of sulfur chemistry is provided here. Because there is a large number of species that can form in the S-O-H system in aqueous solution it is necessary to briefly explain the chemistry of the sulfur-water system to provide a basis for assessing whether or not aggressive species were likely to be present. (A full discussion of aqueous sulfur chemistry is presented in reference 4.) Table IV-1 summarizes the names, structures, and sulfur oxidation numbers of various species that can form in the S-O-H systems. In general, the higher oxidation number species are stable at the more positive (anodic) electrochemical potentials, and the lower oxidation number species at the more negative (cathodic) potentials, but many species are metastable.

SO_4^{--} is the equilibrium species at room temperature in oxygenated water at pH=5 but H_2S (S^{--}) is the stable species if the water is hydrogenated. At intermediate potentials there is a small region where elemental sulfur is the stable form. This region is believed to disappear at higher temperatures but the equilibrium thermodynamics are much less well established at 300°C than at 25°C. Although SO_4^{--} and S^{--} are generally the dominant equilibrium species within the pH and temperature ranges of interest, small equilibrium concentrations of other species also exist. Among these less dominant species are HSO_3^-, $HS_2O_3^-$, and HS_2^-. There are also numerous polysulfide species (S_2^{--}, S_3^{--}, S_4^{--}, etc.) which become more important if the sulfur electrochemical activity is high and the potential is low. In addition to equilibrium species, metastable forms also have to be considered. In the pH range of interest SO_3^{--} can exist at high potentials and $S_2O_3^{--}$ at lower potentials.

Determining the amounts of these species likely to be present in solution is difficult because of lack of knowledge about the kinetics of the various oxidation, reducton, and disproportionate reactions involved. At low temperature, the rate of reduction of SO_4^{--} at low potentials (where it should go to S^{--}) is so slow that SO_4^{--} seems to persist indefinitely. Solutions of $S_2O_3^{--}$ and other metastable oxyanions are also quite stable at room temperature although from equilibrium considerations they should disproportionate to S and SO_4^{--} . Also, oxidation of sulfide (S^{--}) to sulfur is more rapid than further oxidation to oxyanions like SO_3 and SO_4 at room temperature. Kinetic information is sparse at higher temperatures but the data of De (reference 6) seem to indicate that S_2O_3 is extremely electroactive above 150°C and that kinetics of the reactions between the various oxidation states can be described as follows:

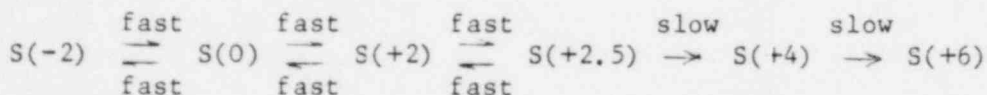$$S(-2) \underset{fast}{\overset{fast}{\rightleftharpoons}} S(0) \underset{fast}{\overset{fast}{\rightleftharpoons}} S(+2) \underset{fast}{\overset{fast}{\rightleftharpoons}} S(+2.5) \overset{slow}{\rightarrow} S(+4) \overset{slow}{\rightarrow} S(+6)$$

TABLE IV-I
AQUEOUS SULFUR SPECIES

Formula	Structure	Sulfur Oxidation Number*	Name
H_2S or $S^=$		-2	sulfide
H_2S_2, $S_2^=$	$[S-S]^=$	-1	polysulfides
H_2S_3, $S_3^=$	$[S-S-S]^=$	-2/3	polysulfides
H_2S_x,	$[S-S--]^=$	-2/x	
S S_8 rings		0	sulfur
$S_2O_3^=$	$\left[O-\overset{O}{\underset{O}{S}}-S \right]^=$	+2	thiosulfate
$S_4O_6^=$	$\left[O-\overset{O}{\underset{O}{S}}-S-S-\overset{O}{\underset{O}{S}}-O \right]^=$	+2.5	tetrathionate
$SO_3^=$	$\left[O-\overset{O}{S}-O \right]^=$	+4	sulfite (sulfurous acid)
SO_2		+4	sulfur dioxide
$S_2O_6^=$	$\left[O-\overset{O\,O}{\underset{O\,O}{S-S}}-O \right]^=$	+5	dithionate
$SO_4^=$	$\left[O-\overset{O}{\underset{O}{S}}-O \right]^=$	+6	sulfate

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* Oxidation number is the formal electrical charge assigned to the sulfur on the assumption that H is +1 and O is -2 in these compounds.

FIGURE IV-1

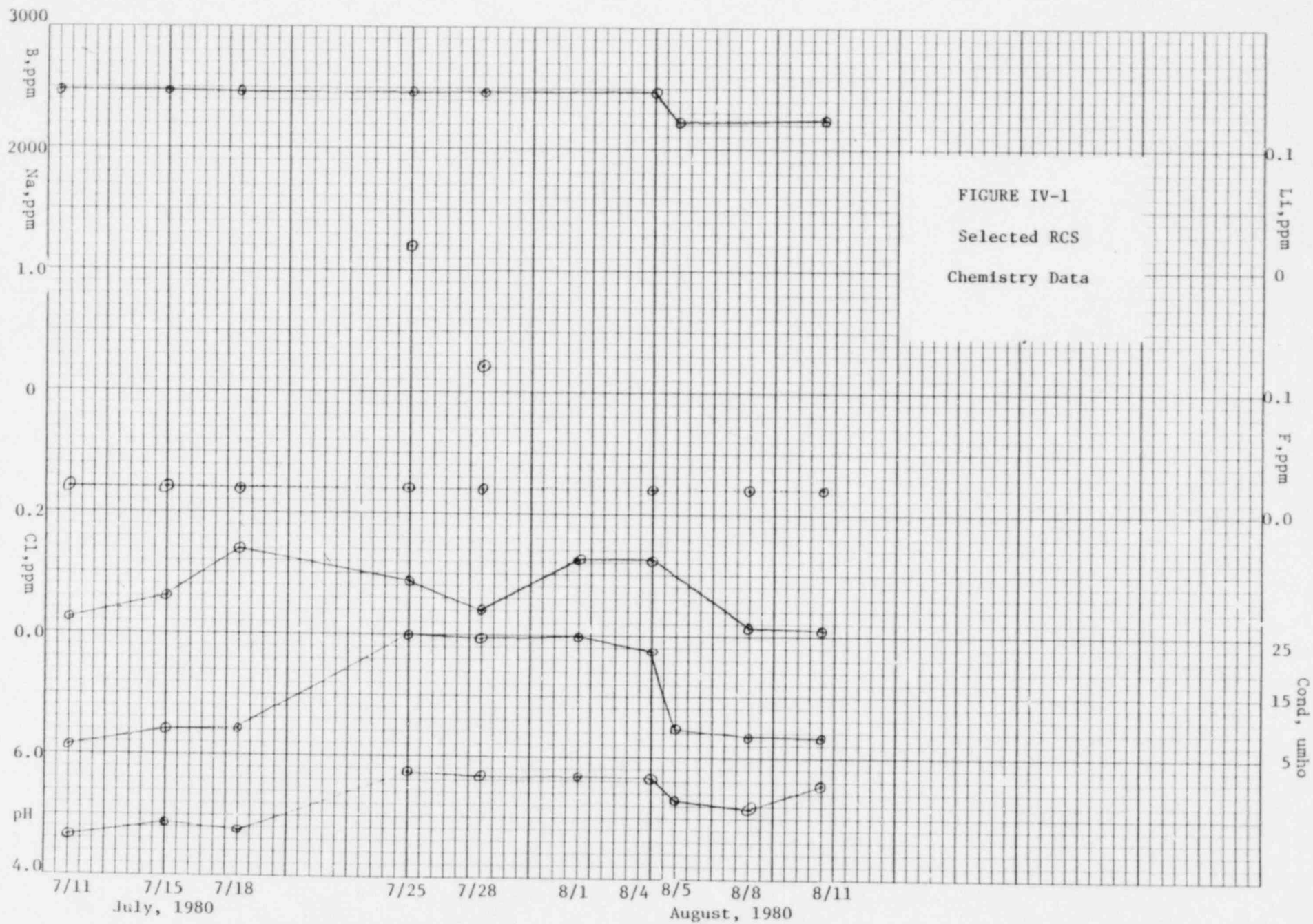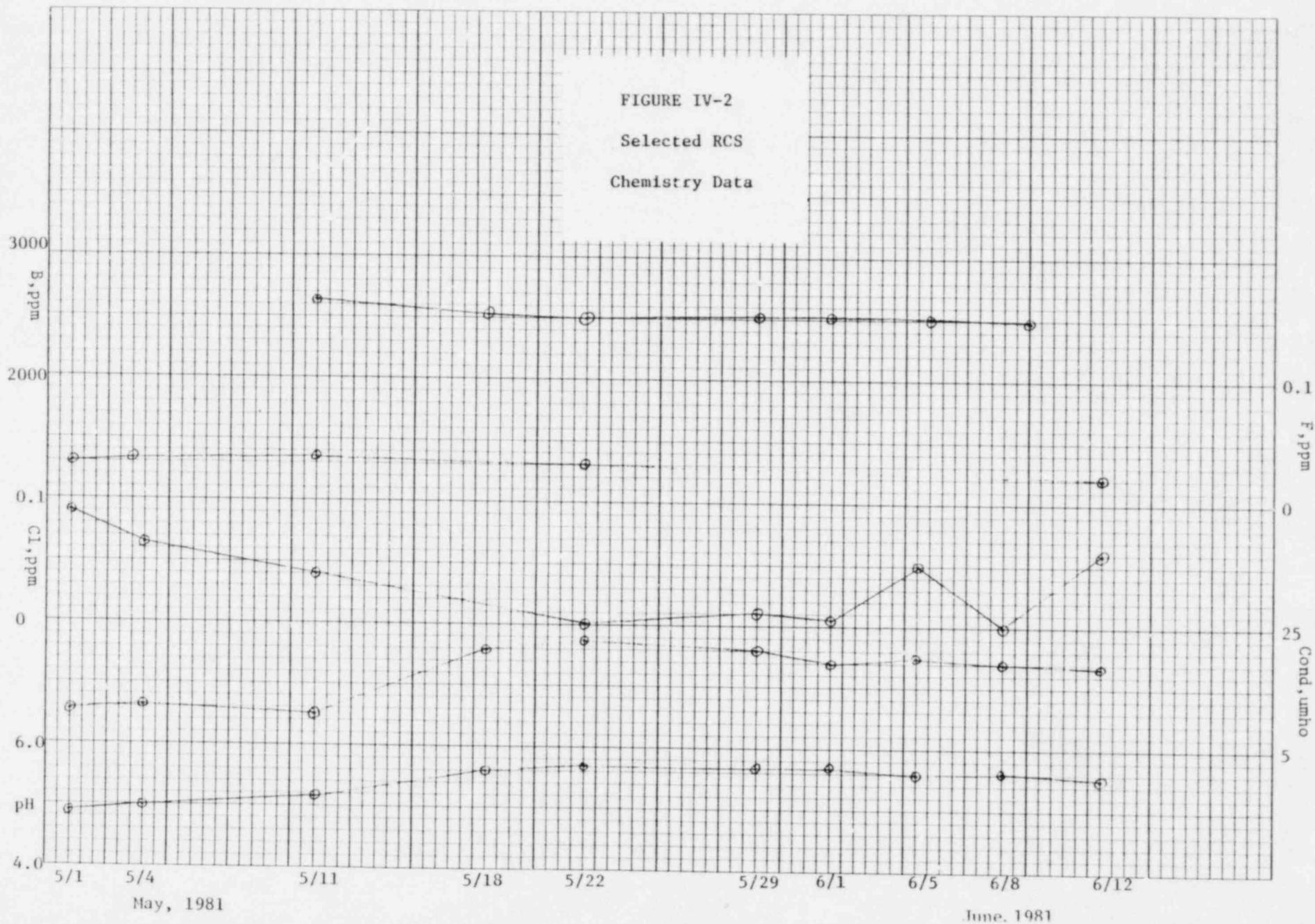Selected RCS

Chemistry Data

FIGURE IV-2

Selected RCS

Chemistry Data

V. OTSG AND PRIMARY SYSTEM CHEMISTRY SAMPLING

A. Wipe Sampling Program

   1. Introduction

      A wipe sampling program was organized to aid in determining con-
      taminant source(s) and concentrations, as well as, to identify
      potential damage mechanism(s) in the TMI-1 steam generators. All
      originally scheduled wipe sampling is complete. Analysis of wipe
      samples collected has been completed for sulfur and chlorine con-
      tent, and for spectrographic analysis.

   2. Wipe Sample Analysis

      A wipe sampling program was initiated to establish the contaminant
      levels in the OTSG's (both primary and secondary side).

      Part of each sample collected was analyzed for chlorine using ASTM
      D-512-67 Method C. These same samples were also analyzed for
      sulfur. Analytic procedures used were such that the sulfur was
      first oxidized to sulfate resulting in a measurement of total
      sulfur present. ASTM D-516-68 Method B Modified was then followed
      to determine sulfur content.

      Finally, some of the collected samples were selected by GPUN/B&W
      for spectrographic semi-quantitative analysis.

   3. Results and Conclusions

      Results of wipe sample analysis are shown in Tables V-1 and V-2.

      Examination of the results of analysis resulted in the following
      conclusions:

      a. Sulfur Concentrations

         1) Tube ID wipe analysis revealed slightly higher con-
             centrations of sulfur in OTSG B than in OTSG A.

         2) Tube ID wipes disclosed primary side sulfate concen-
             trations at the UTS were at least two times as high as
             concentrations at the LTS, in both generators.

         3) Primary side sulfate concentrations, based on OTSG upper
             plenum tube ID samples ranged from 970 to 3600 ug/ft^2.
             Concentrations of sulfate at the primary UTS surfaces,
             with only one UTS wipe sample from each generator in-
             cluded in the data base for subsequent comparison,

indicated concentrations of 770 and 930 ug/ft^2. This compares with levels less than 220 ug/ft^2 measured on the tubes during fabrication.

4) Data indicates presence of sulfur at lower levels on the primary side tube surfaces in the OTSG's, thus there is potential for a sulfur residue on other surfaces in the RCS system. Reference 13 reports the results of an inspection of the RCS.

5) Secondary side sulfur concentrations were generally higher than on the original secondary side tube surfaces after manufacture but before service ranging from less than detectable to 3100 ug/ft^2. See Table V-3 for OTSG-B tube hole ID's data and Table V-1 for OTSG-A data.

b. Chlorides Present

Chloride levels were well below the 1000 ug/ft^2 maximum limit established in the B&W cleaning specifications for RCS surfaces.

c. Additional Sampling

The following wipe samples are presently at LRC in the process of being analyzed.

    6 CRDM Leadscrew samples
    4 RC Bleedtank samples
    1 Vent header sample
    4 Retainer (taken at LRC) wipe samples
    1 Retainer (taken at Site) sample
    1 clean wipe (Blank)
    2 RV O-ring swipes

Preliminary results indicate that sulfur levels similar to these in the OTSG tubes exist in other areas of the RCS.

B. Water Sampling Program

1. Introduction

As a result of the tube damage in the TMI-1 steam generators, a water sampling program was established to provide input to damage mechanism identification and to aid in determining the contaminant source. All currently scheduled water sampling and analysis is completed.

2. Water Sample Analysis

    Analyses performed on fracture surfaces of pulled tubes revealed
    the presence of sulfur. A water sampling program was initiated to
    provide data on sulfur in the RCS and auxiliary systems . The
    method of analysis for sulfur used by B&W on the water sample is
    B&W procedure #718T-75, which is modified ASTM D-516-80 Method B,
    performed after preconcentration to improve sensitivity. This
    procedure is turbidometric determination of total sulfur after
    oxidation with bromine water. The sulfate form of the sulfur
    present may be determined by this method without the oxidation
    step if the concentration of sulfur in the unconcentrated sample
    is higher than about 500 ppb. Reduced sulfur may also be deter-
    mined with a non-specific titration using a standard iodine solu-
    tion. Analysis performed by Westinghouse was by ion chromo-
    tography. Minimum sensitivity of this Westinghouse technique is
    about 50 ppb.

3. Results and Conclusions

    Water sampling efforts began in December when two secondary side
    OTSG samples and one decay heat sample were taken and analyzed.
    The results of these analyses are given in Table V-4. High decay
    heat sample sulfur levels in the December decay heat sample (730
    ppb), plus indications of sulfur in areas of OTSG primary side
    tube defects prompted taking additional RCS/decay heat water
    samples. Twenty-one more water samples were taken in January and
    early February from various locations in the RCS and analyzed by
    B&W. Table V-5 contains the analysis results from these water
    samples. Total sulfur is reported for each sample. When appre-
    ciable levels of total sulfur were reported, (samples from the
    Reactor Building Spray System), reduced sulfur is also reported-
    given as sulfate.

    In March and April, samples were analyzed by Westinghouse. Table
    V-6 contains the analysis results.

    There are a number of comments to be made based on sample analysis
    data:

    a. Water samples from the decay heat system showed sulfur level
        reduction between December and February (.7 ppm - Dec., .4
        ppm - Jan., .1 ppm - Feb.). There is no way to indicate
        what peak RCS sulfur levels were reached prior to sampling.
        Reduction of RCS decay heat sulfur level is attributed to (1)
        flushing of the system lines, (2) dilution as a result of
        leakage from the BWST water into the system and (3) system
        cleanup.

b. RB Spray System sample points all indicated elevated sulfur
    concentrations (14 ppm to 176 ppm as SO_4) much higher than
    other sample points. Solution pH reading were also taken
    from four spray system samples as shown in Table V-8.

    These four samples (Table V-6, #7 through 10) were analyzed
    for reduced sulfur. Significant amounts of reduced sulfur
    were shown in the RB Spray System interconnect lines to Decay
    Heat System (161 ppm – DHA, 4 ppm DHB). Since the RB Spray
    System showed by far the greatest sulfur concentrations of
    samples taken, it is identified as a possible sulfur intro-
    duction point into the Decay Heat System. Also the presence
    of appreciable quantities of reduced sulfur ties in with a
    damage mechanism of sulfur attack at lower temperatures.

c. The caustic mix tank water sample showed 7 ppm sulfate. Due
    to the high ratio of sodium to sulfur, which prevents the
    formation of an acid environment, and due to the dilution
    factors involved, the caustic mix tank proves an unlikely
    source of sulfur contamination to the RCS/Decay Heat system.

d. The ion chromotography results were subject to interference
    and generally yielded more erratic results than the turbidi-
    metric technique. One set of samples in early March was
    contaminated by the lids of the scintillation bottles and
    made unusable.

e. For comparison between the TMI-1 results and industry ex-
    perience, some RCS/Decay Heat water samples were taken from
    other B&W operating units (see Table V-7). These showed
    levels of sulfur below minimum detectable concentrations.

TABLE V-I

WIPE SAMPLE ANALYSIS

Sample#	Date Taken	OTSG	Tube I.D.	Tube Hole I.D.	Tubesheet General Area	Location		Sample Analysis CL (μg/ft^2)	SO$_4$ (μg/ft^2)
1	1/13/82	A	R151T7			Upper Plenum		<70	3000
2	1/13/82	A	R4T2			"	"		
3	1/13/82	A	R1T5			"	"	110	970
4	1/13/82	A	R148T24			"	"		
5	1/13/82	A	R6T14			"	"	<70	2500
6		A	R139T15			"	"	<70	1100
7					NOT TAKEN				
8	1/14/82	B	R3T23			Upper Plenum		<70	2400
9	1/14/82	B	R72T2			"	"		
10	1/14/82	B	R8T22			"	"	<70	3600
11	1/14/82	B	R2T16			"	"		
12	1/14/82	B	R3T11			"	"	<70	3000
13		B	R7ST3			"	"	<70	2300
14	1/14/82	B			W-axis	"	"	56	930
15	1/15/82	A	Near W-axis			Lower	"	<70	<230
16	1/15/82	A	" " "			"	"		
17	1/15/82	A	" " "			"	"	<70	<230
18	1/15/82	A	" Y-axis			"	"	<70	1500

TABLE V-I (Cont'd)   Page 2

WIPE SAMPLE ANALYSIS

Sample#	Date Taken	OTSG	Tube I.D.	Tube Hole I.D.	Tubesheet General Area	Location	CL(ug/ft²)	SO₄(ug/ft²)
19	1/15/82	A	Near Y-Axis			Lower Plenum		
20		A	" " "			" "	<70	580
21	1/15/82	A			W-Axis	" "		
22	1/15/82	A			Y-Axis	" "	10	250
23	1/15/82	B	Near W-Axis			" "	<70	<280
24	1/15/82	B	" " "			" "		
25	1/15/82	B	" " "			" "		
26	1/15/82	B	" " "			" "	<70	1700
27	1/15/82	B	" Z-Axis			" "	<70	<280
28	1/15/82	B	" " "			" "	<70	470
29	1/15/82	B			W-Axis	" "		
30	1/15/82	B			Z-Axis	" "	10	220
31	1/15/82	A		71-126		Upper Plenum	<60	540
32	1/20/82	A		112-7		" "	350	1100
33	1/20/82	A		11-66		" "		
34	1/20/82	A		16-69		" "	350	820
35	1/20/82	A		12-62		" "		
36	1/20/82	A		13-63		" "	<60	<240
37	1/20/82	A		112-5		" "		

TABLE V-I (cont'd)

WIPE SAMPLE ANALYSIS

Sample#	Date Taken	OTSG	Tube I.D.	Tube Hole I.D.	Tubesheet General Area	Location	$CL(ug/ft^2)$	$SO_4(ug/ft^2)$
38	1/20/82	A		112-9		Upper Plenum	350	2200
39	1/20/82	A		68-7		" "		
40	1/20/82	A		88-11		" "	180	3100
41	1/20/81	A		62-8		" "		
42	1/20/82	A		133-74		" "	82	<240
43	1/20/82	A		146-8		" "		
44	1/20/82	A		146-6		" "	380	650
45	1/20/82	A			Y-Axis	" "	63	770
46	1/20/82	A			W-Axis	" "		
47	1/20/82	A		23-93		" "		

Table V-2

EMISSION SPEC RESULTS

	BLANK	#2	#9
Ash Weight (mg), blanked	.9	4.9	3.8
Area Wiped (ft^2)	-	.145	.145

Emmission Spectroscopic Results, %

Compound*	Blank	#2	#9
ZnO	2 wt %	.5 wt %	.5 wt %
Na_2O	1.0	.3	.3
CuO	.1	.1	.2
MoO_3	< .03	.2	.3
V_2O_5	< .03	< .03	< .03
CaO	> 14	4	5
TiO_2	.07	.2	.3
Al_2O_3	.9	.4	.4
CoO	< .03	.03	.03
ZrO_2	.1	.7	.7
Fe_2O_3	1.5	13	17
SnO_2	.08	.1	.1
NiO	< .03	20	23
Cr_2O_3	< .03	15	10
MnO_2	.3	.2	.3
PbO	.03	< .03	< .03
MgO	> 25	1.8	3
SiO_2	> 25	4	5

* Compounds listed are based on standards used.

The form of the elements in the samples may be different.

Table V-2 (Continued)

EMISSION SPEC RESULTS

	BLANK	#19	#24	#33	#43
Ash Weight (mg), blanked	1.0	4.2	1.4	37.4	11.5
Area wiped (ft^2)	–	.145	.145	.170	.170

Compound*	Blank	#19	#24	#33	#43
ZnO	3 wt %	.8 wt %	.8 wt %	<.2 wt %	.2 wt %
Na_2O	.8	.5	.4	<.3	.4
CuO	.2	.1	.2	.03	.08
MoO_3	<.03	.5	.4	.2	.5
V_2O_5	<.03	.05	<.03	<.03	<.03
CaO	>14	4	6	.4	1.8
TiO_2	.07	.9	.5	1.9	.3
Al_2O_3	1.2	.5	.6	.1	.7
CoO	<.03	.06	.05	<.03	<.03
ZrO_2	.1	3	1.3	<.03	<.03
Fe_2O_3	1.5	>25	20	>25	>25
SnO_2	.09	.2	.2	<.03	<.03
NiO	<.03	>25	11	8	10
Cr_2O_3	<.03	25	11	2	?
MnO_2	.3	.5	.4	.8	.7
PbO	.03	<.03	.03	<.03	.03
MgO	>25	2	6	3	1.3
SiO_2	25	4	9	.5	3

* Compounds listed are based on standards used.

The form of the elements in the samples may be different.

Table V-3

TMI -1 WIPES (DECEMBER 1981)

TUBE HOLE ID'S AT UTS
OTSG B

SAMPLE	TUBE	DEPTH WIPE TAKEN	SO_4 (ug/ft^2)
1.	8-25	3 in.	2800
2.	8-25	8 in.	3300
3.	10-25	3 in.	1900
4.	11-23	3 in.	2800
5.	11-23	8 in.	2000
6.	33-30	8 in.	2000

Table V-4

TMI-1 WATER SAMPLES

FOR TOTAL SULFUR

ANALYTICAL RESULTS

SAMPLE	TOTAL SULFUR AS SULFATE (ppm)
RCS	.7
OTSG-A	.3
OTSG-B	.3

SAMPLES TAKEN 12/01/81

Table V-5

TMI-1 WATER SAMPLES
ANALYTICAL RESULTS

SAMPLE	DATE TAKEN	TOTAL SULFUR (ppm) (AS SULFATE)	REDUCED SULFUR (ppm) (AS SULFATE)
1. Decay Heat A	1/18/82	.4 PPM	*
2. Decay Heat B	1/18/82	.4 PPM	*
3. Core Flood A	1/19/82	<.1 PPM	*
4. Core Flood B	1/19/82	<.1 PPM	*
5. Spent Fuel Pool	1/18/82	.4 PPM	*
6. Borated Water Recir. Pump Discharge	1/20/82	.3 PPM	*
7. R.B. Spray Pump Inlet	1/20/82	14 PPM	<1
8. R.B. Spray Pump Outlet	1/20/82	15 PPM	1
9. R.B. Spray System Inter-Connect to D.H.A.	1/20/82	176 PPM	161
10. R.B. Spray System Inter-Connect to D.H.B.	1/20/82	14 PPM	4
11. Make-Up Pump Outlet A	1/20/82	<.1 PPM	*
12. Make-Up Pump Outlet B	1/20/82	.3 PPM	*
13. Caustic Mix Tank	1/20/82	7.0 PPM	**
14. Lithium Hydroxide Mix Tank	1/20/82	<.1 PPM	*
15. Boric Acid Mix Tank	1/19/82	<.1 PPM	*
16. Borated Water Storage Tank	1/20/82	<.1 PPM	*
17. Demin. Water Storage Tank	1/19/82	<.1 PPM	*
18. Reclaimed Water Storage Tank	1/19/82	<.1 PPM	*
19. Bleed Hold-Up Tank B	1/19/82	<.1 PPM	*
20. Bleed Hold-Up Tank C	1/20/82	<.1 PPM	*
21. Decay Heat Removal A	2/4/82	<.1 PPM	*
22. Control Sample		<.1 PPM	*

* Not Analyzed Due To Low Concentration.
** Not Analyzed Due To High Caustic Concentration.

Table V-6

ION CHROMOTOGRAPHY RESULTS

SAMPLE POINT	DATE	SO_4 ppb	REMARKS
Decay Heat A	3/18	123	
IWT Mixed Bed	3/17	246	
Precoat A inlet	3/17	246	
Precoat A outlet	3/17	(Interference Peak)	
Bldg. Spray Pump A inlet	3/17	2465	Pre-Flush
Bldg. Spray Pump B inlet	3/17	(Interference Peak)	Pre-Flush
Bldg. Spray/BWST Line	3/18	822	Pre-Flush
Bldg. Spray Pump A outlet	3/18	2493	Pre-Flush
Bldg. Spray Pump B outlet	3/17	2876	Pre-Flush
Bldg. Spray Pump A inlet	3/20	752	Post-Flush (2.5 Volumes)
Bldg. Spray Pump B inlet	3/20	656	Post-Flush (2.5 Volumes)
Bldg. Spray/BWST line	3/20	64	Post-Flush (2.5 Volumes)
Bldg. Spray Pump A outlet	3/20	546	Post-Flush (2.5 Volumes)
Bldg. Spray Pump B outlet	3/20	764	Post-Flush (2.5 Volumes)
Pre-coat A inlet	3/20	149	end of third run
Pre-coat A outlet	3/20	74	end of third run
BWST	1/20	257	repeat on sample analyzed by B&W
Spent Fuel pool	1/18	559	repeat on sample analyzed by B&W
Decay Heat A	2/4	211	repeat on sample analyzed by B&W
Precoat A inlet	3/23	161	Fourth run

Table V-6 (Continued)

ION CHROMOTOGRAPHY RESULTS

SAMPLE POINT	DATE	SO$_4$ ppb	REMARKS
Precoat B outlet	3/23	416	Fourth run
Bldg. Spray Pump A	4/1	369	Post-Flush (6 Volumes)
Bldg. Spray Pump B	4/1	269	Post-Flush (6 Volumes)
Bldg. Spray Pump A inlet	4/1	1400	Post-Flush (6 Volumes)
Bldg. Spray Pump B inlet	4/1	276	Post-Flush (6 Volumes)
Bldg. Spray/BWST line	4/1	269	Post-Flush (6 Volumes)

Table V-7

WATER SAMPLES

TOTAL SULFUR ANALYTICAL RESULTS

SAMPLE	TOTAL SULFATE AS SULFATE (ppm)
Oconee 1 RCS [1]	< .1
Oconee 3 RCS	< .1
Another B&W Unit: [2]	
RCS	< .1
RCS	< .1
Make-up	< .1
Make-up	< .1
Decay Heat Cooler Outlet	< .1

(1) Analysis completed March 12, 1982

(2) Analysis completed March 3, 1982

VI METALLURGICAL EXAMINATIONS

A. Introduction

In order to positively identify the cause of steam generator tube
failure, extensive metallurgical examination of tube samples removed from
both OTSG's was conducted by Babcock & Wilcox and Battelle Columbus
Laboratories. The laboratory investigation was intended to identify the
failure mechanism, extent of tube damage, and possible environmental
factors contributing to the failures. The metallurgical examinations
together with the results of the primary system water chemistry analysis
(Section V) suggest that the OTSG tube cracking initiated from the primary
side and is a manifestation of sulfur-induced intergranular stress
assisted cracking (IGSAC). Accordingly, a brief review of current
knowledge relating to sulfur-induced IGSAC is presented here to provide a
basis for the subsequent discussion.

B. Attack of Inconel 600 by Water Containing Dissolved Sulfur Species

1. Industry Experience

A state-of-the-art review of relevant industry experience of attack
of Alloy 600 by aqueous environments containing dissolved sulfur species
has been performed for EPRI by several EPRI contractors (Reference 4). A
number of nuclear plants have experienced steam generator tube cracking
problems attributed to the introduction of sulfur species into the
secondary system; also tube pitting, intergranular attack, and wastage
have been observed in pot and model boiler tests in which sulfur species
were present in the form of ion exchange resins. IGSAC of steam generator
tubes initiating from the primary side has also been observed in several
plants but these have been attributed to pure water cracking ("Coriou
cracking") rather than to sulfur-induced attack. The only instances of
IGSAC due to sulfur-contaminated primary-type water uncovered by the EPRI
review were in sensitized Type 304 stainless steel rather than Inconel
600 -- both TMI-1 and ANO-1 have experienced IGSAC in their spent fuel
pools and associated borated water piping and these cases of IGSAC have
been attributed to contamination by sodium thiosulfate.

2. Laboratory Studies

Laboratory studies have shown that Inconel 600 can be very
susceptible to IGSAC at ambient temperatures (25-100°C) in the presence
of metastable sulfur oxyanions such as tetrathionate or thiosulphate. The
susceptibility increases with increased sensitization (i.e., decreased
grain boundary chromium content), increased temperature (at least up to
80°C), and decreased solution pH. For highly sensitized material the
crack growth rate can be extremely fast even in dilute solutions - a rate
of about 1mm/day has been reported at 80°C in a solution containing 0.7
ppm S as thiosulfate (Reference 5). The mechanism of cracking is not
completely understood but susceptibility appears to be restricted to a
narrow range of electrochemical potentials that correspond to the region

of thermodynamic stability of atomic sulfur (see Section IV). This suggests that the mechanism of cracking may involve interaction between atomic sulfur and the bare metal at the crack tip. Under freely corroding conditions near room temperature, aeration of the solution is required to raise the electro-chemical potential into the cracking range. However, it is not clear that aeration would be required for cracking at higher temperatures where it has been observed that thiosulfate is highly electroactive and that elemental sulfur can be produced at a significant rate by disproportionation (Reference 6). There is also evidence of a synergistic effect on cracking susceptibility for the copresence of chloride ions and sulfur oxyanions (Reference 7) and very recent results (Reference 5) suggest that the presence of lithuim hydroixide may inhibit cracking in borated water environments.

3. Acidic Sulfate

IGSAC of Inconel 600 can also occur at high (greater than 300°C) temperatures in acidic sulfate environments. The mechanism in this case seems to be related to that of IGSAC in pure water and caustic environments in that susceptibility to cracking is not associated with the degree of sensitization of the Inconel. In slightly acidic or neutral solutions, high potentials are required to induce IGSAC in sulfate solutions. These potentials are unlikely to be attained in the reducing environment present in the primary system of a PWR at high temperatures so it is not probable that acid sulfate cracking would be the cause of tube failures initiating from the primary side.

4. Key Observations

The key observations identified by the EPRI review can be summarized as follows:

a. IGSAC of Alloy 600 in sulfate-containing water has been observed at operating temperatures (300°C) in laboratory tests but is unlikely to occur under PWR primary system conditions.

b. IGSAC of Alloy 600 in water containing sulfur oxyanions such as thiosulfate has been observed at low temperatures (25-100°C) in laboratory tests under conditions that are more likely to occur in the PWR primary system. Cracking is very rapid and susceptibility depends on degree of sensitization, pH, temperature, and electro-chemical potential.

c. Plant and model boiler experience is entirely related to secondary side problems. None of the previous plant occurrences of primary side IGSAC of Alloy 600 tubing have been attributed to attack by sulfur species.

C. Description of Samples Taken

After identification of the leaking OTSG tubes by Nitrogen bubble testing, it was decided that in order to determine the cause of failure, tube samples would need to be removed from the steam generators for analysis. The initial selection of tube samples was made after eddy current testing had been commenced and the choices were made based on maximizing the number of defect indications in each tube and providing an adequate sample of eddy-current signals for eddy-current qualification.

Four tubes were initially selected from the "B" generator. One (1) tube was a known leaker from the bubble test results (B11-23), the other three tubes contained eddy-current indications with greater than 80% through wall penetration. Three of these samples were twelve (12) inches in length with the top 5/16" removed during the pulling operation. These samples are designated as short pulls. In addition to these three short pulls, a sample approximately sixty (60) inches in length was also pulled. In this case, the top two (2) inches were removed during the tube pulling operation. This sample and others which were in excess of twelve (12) inches were designated long pulls.

After the initial samples had been removed, it was later discovered that eddy-current signal anomalies were showing up at the roll transition region. In order to determine the disposition of these tubes, additional tube samples were selected for removal which contained these eddy-current signals. This time, fifteen (15) tubes were removed from the "A" generator. Three (3) tubes were long pulls and twelve (12) were short pulls. The designation of these tubes is contained in Table VI-1, along with the laboratory which performed the failure analysis on each tube.

D. Failure Analysis Program

B&W Lynchburg Research Center and Battelle Columbus Laboratories were assigned a multi-task program to provide information related to the steam generator tube damage problem. This program contained the following analyses/examinations:

1. Visual Examination

This included an initial on-site visual examination of the first four (4) tubes pulled as well as a detailed visual examination at the laboratories. The on-site examination was designed to provide quick feedback as to the extent of damage and characterization of the failure mechanism.

2. Eddy-Current Examination

Eddy-current examinations were performed after tube removal, both on-site and at the laboratories. These examinations were conducted to determine if any signal changes occurred due to the tube being out of the tubesheet, and also to more accurately locate the defects.

3. Radiography

Radiography was performed on the tube samples to determine if incipient defects could be detected which may have been missed by eddy-current.

4. Sectioning and Bending

In order to locate cracks which could not be seen visually, sections of tubes containing eddy-current signals were split into longitudinal segments and bent around a mandrel to open up defects.

5. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX)

SEM analysis was conducted on the fracture surfaces to provide details on fracture topography at magnification up to 5,000 X. EDAX analysis, which is conducted in conjunction with the SEM analysis, is used to determine the qualitative elemental composition of deposits observed on the tube surfaces.

6. Auger Electron Spectroscopy (AES)

AES analysis was performed on surface films to determine the quantitative elemental composition of these films at various depths through the films.

7. Electron Spectroscopy for Chemical Analysis (ESCA)

This surface film analysis technique was used to determine the compound form of various contaminants and metallic elements present on the tubing.

8. Electron Diffraction

Bulk surface analysis techniques for compound identification.

9. Sodium Azide Spot Test

This spot test provided a qualitative assessment as to whether reduced sulfur species were present at the tube surfaces.

10. Metallography Microstructural Analysis

This analysis was used to assess crack morphology as well as define the grain structure and carbide distribution.

11. STEM, EPR and Huey Testing

These techniques were utilized to assess the degree of chromium depletion in the grain boundaries and hence, the degree of sensitization as it relates to material susceptability to intergranular corrosion.

12. Residual Stress and Plastic Strain

The X-ray technique was utilized to provide a stress profile in the roll and roll transition region.

13. Tension Testing

14. Hardness Testing

15. Dimensional Measurements

E. Eddy-Current Verification

Nineteen tubes have been removed from the two OTSG's to date. These tubes were chosen to contain a complete sampling of the types of defects being found by eddy-current and as such are not a representative sample of the entire tube population. That is, the samples were all located in the outer periphery of the tube bundles and all contained multiple defects when in reality, the majority of defective tubes have cracks only at the roll transition or in the top 1/4" of the tube.

The sampled tubes contained 97 NDE indications as shown on Table VI-2 (the top and roll transition of one tube was removed prior to pulling).

Defects in the 0-1/4" location were detected either visually or by radiography, as the eddy-current technique utilized at that time was was not capable of detecting defects at the end of the tube in rolled and welded regions. Subsequent developments in eddy-current, however, later permitted examination of that region.

Defects in the other locations were detected by eddy-current and are considered verified when a crack is detected by either visual examination or laboratory bending of a strip with the I.D. in tension.

All eddy current indications tested in the laboratory were found to be associated with a tube anomaly, with the vast majority being cracks.

In the roll transition region, 8 out of 9 indications tested in the laboratory were found to be cracks; one was located at a pite. Below the roll transition, 26 of 29 indications were found to be cracks; details of the other tube anomalies are noted in Table VI-2.

The nineteen samples consist of approximately 38 feet of tubing. Samples removed for metallurgical testing to the present time represent approximately 14 feet of this tubing. No instances were noted in this tubing in which a defect was identified which was not previously noted during eddy-current testing.

Since a one-to-one correspondence between eddy-current indications and tube wall defects has been demonstrated in the laboratory, it may be concluded that eddy-current results are a fair representation of the

distribution of tube defects below the top 1/4" of the tube. This conclusion must be qualified in that eddy-current signals of less than about 1 volt are only about 75% repeatable. Reference 9 reports the details of eddy-current testing.

F. Crack Characterization

The intergranular stress corrosion cracks have been observed to proceed from the I.D. of the tube, assuming a "thumbnail" shape with an aspect ratio of 2 to 3 (See Figure VI-1). The cracks appear to be oriented in a circumferential plane. Some of the larger cracks tend to have a slight spiral as they propagate around the tube. In several instances, multiple circumferential cracks have been found at the same axial location on the tube. The detailed characterization of all the examined cracks is reported in Reference 10.

In general, the cracks were extremely tight and not visible either with light microscopy under low power magnification (30X) or high power magnification (500X) in the SEM. Also, in some cases, cracks were associated with visible reddish brown surface deposits while in other cases there were cracks present with no visible surface deposits other than the overall surface oxide film.

Of the 30 verified cracks not in the top edge or roll transition areas, 8 were visually detected on O.D. of the tube, suggesting that stable crack growth can occur past the point of wall penetration. Even beyond wall penetration, the crack tends to maintain the slant-sided configuration; both field experience and experimental work tend to support this view.

Table VI-3 compares eddy-current results with actual wall penetrations for the defects in the sampled tubes. The vast majority of the defects have proceeded completely through the wall - this ranges from just barely through (not visible on the tube outside surface) to a visible outside surface crack extending 90° or more. The corresponding eddy-current depth call is generally less on the average. This suggests that an eddy-current indication showing significant depth should be considered a crack that is already through-wall.

The unverified eddy-current indications have similar indicated through-wall penetrations to those already verified. These indications are also likely to be cracks that are or completely or nearly through the tube wall.

Circumferential cracks were found within 1/4" of the top of the tube in 8 of the tubes. These cracks were not detectable with the eddy-current technique originally used, and were found in the laboratory by bending or radiography. Eddy-current techniques have since been developed to inspect the top 1/4" of the tube and detect these defects. The circumferential cracks ranged from 60° to 360° in extent. In two cases, small axial cracks linked the circumferential cracks to the tube ends.

G. Metallography

All metallographic examinations performed on tube samples removed from TMI steam generators have shown the microstructure to be consistent along the length of the tube and on different tube samples (see Table VI-4 for locations). The microstructure consists of discrete chromium carbide in the grain boundaries with a moderate dispersion of carbide within the grains (Figure VI-2). This microstructure is typical for tubing material used in B&W steam generators and is representative of their mill-anneal plus stress relief heat treatments. The microstructure, however, does suggest that the material could be sensitized.

Metallography in regions showing eddy current defects has provided some interesting data. In all cases, microspecimens prepared in regions where eddy current indications were found, have in fact, uncovered cracks. In most cases cracks were not visible to the naked eye or visible under scanning electron microscopy, although there were cases where cracking was severe enough that it was visibly observable. In these two different circumstances it appears that the degree of intergranular attack associated with the cracks is different. That is to say, for major cracks where crack extent was significant and cracks were open, there generally tended to be regions of intergranular attack on either side of the crack 10 to 20 grains wide and through the wall in penetration. In most cases, however, where cracking was very tight and very limited in extent, the degree of intergranular corrosion was significantly less. In addition, metallographic specimens made in areas away from cracks where deposits have been observed in a few cases, showed some very small areas of localized IGA. In general, these areas did not exceed 5 mils in depth and no cracks were associated with these areas. Regardless of the area examined, no cracks were ever detected where eddy current signals were not present.

Variations in grain size do exist, however the distribution is random throughout the microstructure and there were no changes detected through the tube wall thickness. There is typically a 0.8 to 1.2 mil grain site. The only exception to this is in the rolled regions where the grains on the inside surface did show deformation from the rolling process but only to the limited depth expected.

The carbide morphology and grain size suggest that the tube approached 1900°F during the final mill anneal. At this temperature, significant quantities of carbon are dissolved and available for precipitation at the grain boundaries during the final stress relief.

H. Sensitization

As previously noted, the carbide morphology in the microstructure suggests that the tube material could be in the sensitized condition. Several different techniques were used to check for sensitization and quantify its extent.

Samples from one tube were subjected to the modified Huey test frequently used on Inconel. Attack at the grain boundaries was so severe that a valid weight loss measurement could not be made. Qualitatively, however, the material was highly sensitized.

Electrokinetic Potentiostatic Reactivation (EPR) testing performed on samples from three of the tubes gave peak potentials of 110 to 125 mV, indicating a severe degree of sensitization.

Scanning Transmission Electron Microscopy (STEM) was used to measure the chromium level at the grain boundaries of samples from actual tubing, archive material in the mill annealed condition, and archive material that had received a simulated stress relief treatment. Both the actual tubing and the stress relieved archive material exhibited severe sensitization. Chromium levels were 5-8% near the grain boundary. Levels below approximately 10% render the material susceptable to intergranular attack as suggested by G. P. Airey (Reference 8). Archive material in the mill annealed condition, however was not significantly sensitized and exhibited chromium levels above 10%.

I. Surface Analysis

Following bending at the eddy-current locations (putting the I.D. in tension) in order to open up the cracks for observation, energy dispersive X-ray analysis (EDAX) and scanning electron microscopy was performed on the fracture surfaces of many samples. In addition to confirming the intergranular nature of the cracks, surface chemistry was also analyzed to determine the presence of any corrodant.

To date, EDAX analysis has shown sulfur to be the primary contaminant present on the fracture surfaces. Chlorine has also been observed in random locations but some of this is believed to be handling contamination.

In addition to looking at the fracture surfaces with EDAX, the I.D. surfaces of the tubes were also examined by this technique. This examination showed sulfur to be one of the contaminants present on the surface. The sulfur was not uniformly distributed but in general it was present as a major contaminant.

In addition to the EDAX analysis, Auger analysis of surface films was also performed. This analysis again found sulfur to be one of the major contaminants, however, carbon was present in large quantities (50-90%) on the as-received surface. This carbon is reported to be in several forms either as a hydrocarbon, a carbonate or graphite carbon. The analyses indicated, however, that the carbonate was present mostly on the surface and as you sputtered to greater depths through the oxide layer the carbon deeper in the oxide appeared to be present as a hydrocarbon.

Sulfur levels measured by Auger analysis range from approximately two atomic percent to eight atomic percent. This sulfur was identified in the oxide up to 4,500 A in depth, at which time the percentage had decreased to around 3.2 atomic percent. The analysis for chloride typically indicated chloride was present as less than 1 atomic percent and generally in the range of .2 to .6 atomic percent.

In addition to these contaminants, typical metallic elements expected such as nickel, chromium, iron, were also observed. Normal trace amounts of fission products such as cesium, beryllium, boron and zirconium were also observed (Table VI-5).

In order to determine the form of some of the metallic elements on the fracture surface, ESCA analysis was utilized to identify some of the compounds present. Typically, iron was present as an iron hydroxide $FeOOH$, chromium as the oxide Cr_2O_3, and nickel has been observed as a nickel oxide NiO, nickel hydroxide $Ni(OH)_2$, and a nickel sulfide Ni_2S_3. The latter suggests at least some of the sulfur is combined with nickel, possibly as a complex nickel sulfide. At the surface of the film, significant quantities of nickel sulfate have been detected; deeper into the film, the nickel-sulfur compound is primarily nickel sulfide.

Significant variation exists in the levels of sulfur from point to point, even at the same elevation on the same tube. Nevertheless, it appears that the sulfur contamination is present in significant quantities in several possible forms. They are:

o sulfate as nickel sulfate
o sulfide with nickel, possibly as a reduced form of nickel sulfide
o in a spinel FeO structure with S substituted for O and Ni for Fe in significant quantities.

In order to determine the distribution of contaminants along the length of the tube and the upper tubesheet region, discrete analyses were performed on the I.D. surface. In the top five (5) inches of the tube, samples were taken every half inch and analyzed by both Auger and ESCA. In addition, samples were then analyzed from a location approximately 10 inches and 25 inches from the top of the tube. This analysis showed that the sulfur concentration along the length of the tube generally remained constant. There may have been a slight decrease with distance, however, from the top of the tube depending on the accuracy of the data (Figure VI-3). There were differences noted in the level of concentration of sulfur on I.D. surfaces between different tubes. In addtion, the Auger analysis showed that there was a general increase in nickel concentration and chromium concentration with distance from the top of the tube. This increase in nickel and chromium would suggest a decreasing film thickness with depth.

All surface analysis data to date, therefore, suggests that sulfur is the primary cracking agent and that it is necessary and responsible for the intergranular attack. The question as to whether or not the mechanism

can be reactivated still is unanswered. However, cracking testing does suggest that at this time it is not active.

J. Mechanical Testing and Residual Stress Measurements

Hardness traverses made in the roll regions indicated a maximum hardness on the order of 270 DPH (Tables VI-6 and VI-7). It was interesting to note, however, that this maximum hardness value typically occurred 4 mils in from the I.D. surface and was in fact a peak hardness with values dropping off rapidly as you go further into the tube wall. Hardness midway through the wall would generally be in the order of 190 to 200 DPH which is typical for mill-annealed and stress relieved material. This is also the range of hardness which was measured below the roll transition. For comparison purposes, a fully hard Inconel tube would have a hardness somewhere in the range of 300 to 310 DPH. The data tells us that although the surface may be heavily cold worked, there is metal at mid-thickness that is at lower hardness values and consequently possesses original ductility.

Although cracking has most definitely been observed in the roll region, it does not appear that the rolling process produces any preferential attack. This fact is somehwat confirmed by the results of residual stress measurements made in the roll regions. There was generally a relatively uniform level of plastic strain and residual stress on the inner surface of the tube and there were no stress peaks observed which would correlate directly with cracking locations (Figures VI-4 and VI-5).

Wall thickness measurements were also made and these indicate that wall thinning was on the order of one (1) mil (Table VI-8).

Three tube tensile tests were run from material from two clean areas of tubing and one on a tube containing a defect. The results of these tensile tests indicated that the material from the clean area still meets original mechanical property specifications and that there was no evidence of incipient defects associated with those tested specimens (Table VI-9). The tensile test on the defective tube shows that with a defect through wall for one quarter of the circumference, the tube can still withstand design basis loads.

K. Material Chemistry Analysis

Two pieces from sampled tubes were analyzed for bulk chemical composition. Results of this analysis, shown in Table VI-10, indicate that the material meets the chemical specifications in ASTM SB-163 for Inconel 600 type material.

L. Effects of Heat and Heat Treatment

Analysis of computer plots of total and defective tube locations on a per-heat basis led to the conclusion that the overall defect level of a heat of OTSG tubing is determined by the location of the tubes in the generator. Heats showing good overall performance had a large number of tubes in areas with few defects; poor heats were concentrated in bad areas.

The effect of heat chemistry was analyzed using a calculated residual chromium parameter which represented the available chromium in the matrix after complete carbide precipitation. A small secondary effect of chemistry on performance was observed; it is, however, so small that it is of little practical significance.

Analysis of the full vessel stress relief records indicate that all the tubing in both OTSGs would be expected to be significantly sensitized.

M. Conclusions

1. The tubing has failed due to stress assisted intergranular attack. This has led to through wall penetrations and circumferentially oriented cracks. In all cases, cracks have initiated on the inside surface as supported by the following observations.

    a. Longer crack length on the inside surface than the outside surface when cracks are completely through the wall.

    b. Non-through wall cracks are visible on inside surfaces but not on ouside surfaces.

    c. Bend samples with the inside surface in tension have opened up cracks while bend samples with the outside surface in tension have not opened cracks.

    d. Eddy-current indicates the cracks are originating on the inside surface.

    e. The general crack shape is thumbnail shaped with the apex at the O.D., showing definitely that the cracks have originated on the I.D.

2. The intergranular cracking morphology has been confirmed by both Metallography and Electron Microscopy.

3. Transmission Electron Microscopy has also confirmed that no secondary modes of failure is associated with the intergranular corrosion, that is, no evidence of any low or high cycle fatigue was observed on these fracture surfaces.

4. Some general intergranular attacks not associated with I.D. cracking has been observed. These "islands" of IGA are in general associated with I.D. deposits. IGA found at crack locations tend to involve more penetration in terms of grains (depth) compared to the 6 grains of penetration typical of the IGA "islands."

5. Analysis of surface films on fracture surfaces and on the I.D. surface of the tubing indicate that sulfur is present up to levels of eight atomic percent. The form of sulfur is believed to be either in the form of a nickel sulfide, Ni_2S_3 or some other reduced form of sulfur. It is the presence of the reduced sulfur form that is responsible for the cracking mechanism and without such a contaminant the cracking would have not occurred.

6. Microstructural evaluation of the tubing from numerous locations, has indicated that the structure is representative of that normally expected for steam generator tubing. However, tests have concluded that the material is in a sensitized condition and hence is expected to be susceptible to intergranular attack.

7. To date, all visual, metallographic or bend specimens performed in clean regions of the tubing, that is regions where no eddy-current indications were recorded, all show the tubing to be free of defects in those areas. In addition, all examinations performed at locations where absolute eddy current probing indicated a nearly through will or through wall defect has confirmed the presence of cracking in those regions. To date, the results of correlations between metallographic and eddy current results have shown a one to one correlation.

8. Although there is excellent correlation between eddy-current indications and metallography, it has also been learned that eddy current signals of 80 to 90% through wall, in most instances, actually represent 100% through wall defects.

9. In all cases to date, cracks which have been examined either by metallography or by bend testing, have shown the defects to be at least 90% and generally 100% through wall in penetration. This would suggest that crack growth rates are rapid and that defects, once initiated, propagate to through wall.

10. Auger and ESCA analysis have shown the presence of carbon, sulfur, nickel, chromium, oxygen and sulfur on the fracture surfaces. In addition, normal trace amounts of fission products have been observed. The important results from this analysis have shown that sulfur concen- trations along the I.D. surface of the tubing down to the 27 inch point, are generally uniform with a slightly decreasing level as you go down the tube sample. The significant presence of oxygen also confirms that oxygen was definitely available for the corrosion reactions and that very possibly played a major role for the failures observed.

11. The consistent circumferential orientation of the cracks indicates that a longitudinal stress is part of the cracking mechanism. Residual stresses in the roll alone were not responsible for the cracking. Therefore, the fact that the cracks occurred when the tube was under applied axial tension rather than a hoop stress, suggest the cracks formed during cooldown or in the cold shutdown condition.

12. The observed patterns of failure within each OTSG cannot be explained on the basis of tube heat chemistry or differences in sensitization due to full vessel stress relief; all tube heats are susceptible in areas of significant failure, and all saw essentially the same sensitization conditions during stress relief.

TABLE VI - 1

TUBE SAMPLES EXAMINED

"A" OTSG

TUBE NUMBER	HEAT NO.	SAMPLE LENGTH	INVESTIGATING LABORATORY
13-63	M2408	Long	B & W
71-126	M1671	Long	Battelle
133-74	M2408	Long	B & W
112-7	M2560	Short	B & W
88-11	M2626	Short	Battelle
112-9	M2626	Short	B & W
146-8	M2404	Short	Battelle
112-5	M2560	Short	Battelle
16-69	M2345	Short	B & W
12-62	M2345	Short	B & W
62-8	M2560	Short	B & W
88-7	M2560	Short	B & W
11-66	C2690	Short	B & W
146-6	M2560	Short	Battelle
23-93	M2409	Short	Battelle

"B" OTSG

33-30	M2867	Long	B & W
8-25	M2709	Short	Battelle
11-23	M2320	Short	Battelle
10-29	M2709	Short	B & W

TABLE VI - 2

DEFECT SUMMARY

MAY 11, 1982

LOCATION OF DEFECT	TUBES EXAMINED	NDE INDICATIONS	INDICATIONS EVALUATED	CRACKS VERIFIED	NO CRACKS FOUND
0-1/4" LOCATION	18	13	8	8	0
ROLL TRANS. CRACK	18	10	9	8	1 (NOTE 1)
CIRCUMFERENTIAL CRACK NOT IN TOP EDGE, ROLL TRANS. WITHIN UTS	19	68	29	26	3 (NOTE 2)
CIRCUMFERENTIAL CRACKS BELOW UTS	4	6	4	4	0

NOTE 1 - 1 AREA - ID PITS

NOTE 2 - 1 AREA OF IGA W/O CRACK

       1 10-30% E.C. INDICATION - NO VISUAL DEFECT

       1 MECHANICAL DAMAGE

TABLE VI - 3

DEFECT DEPTH

Location	Visual/Bend Verified		Corresponding EC Data		Untested EC Indications	
	No.	Avg. Penet.	Avg. Penet.	Range of Penet.	No.	Range of Penet.
0-1/4"	9	99%			1	95%
Roll Region	2	100%	95%	95%	10	60-95%
Roll Transition	7	100%	90%	65-95%	2	95%
Roll Transition - 12 in.	10	100%	93%	50*-100%	29	59-95%
12-16 in.					3	80-100%
16-24 in.					4	90-95%
Below UTS lower surface	3	100%	92%	90-95%	1	90%

* - Standard differential probe data
  Other EC data 4 x 1 absolute

TABLE VI - 4

METALLOGRAPHY

X - EXAMINED

O - TO BE EXAMINED

AXIAL LOCATION FROM TOP OF TUBESHEET	A146-8	A133-74	A62-8	A71-126	A13-63	A146-6	B8-25	B33-30	B11-23
0-2	X	X			X	X	X		
2-4	X					X			X
4-8	X								
8-24	X	X	X			X		X	
24-50		X			X			X	
50-70				X				X	

TABLE VI - 5

RESULTS OF AUGER/ESCA ANALYSIS

SPECIMEN 8-25-3 CRACK AND FRACTURE

Element	As Is	ESCA Analysis, %	
		600 A Sputtered	1500 A Sputtered
Cu(a)		4.6	6.6
Ni		3.0	3.4
Fe		1.7	2.3
Cr		1.1	1.5
O	~10	11.1	11.8
Ru		--	0.9
Ag		2.7	0.3
C	>90	75.8	64.8
S		--	0.4
Cs		--	0.4
P		--	0.5
Be		--	7.2

(a) Cu mainly from copper holder

TABLE VI - 6

HARDNESS MEASUREMENTS NEAR TOP
OF B-GENERATOR SAMPLE 10-29

DISTANCE FROM TOP. INCHES	1-1/2 MILS FROM INSIDE SURFACE	MID-WALL	1-1/2 MILS FROM OUTSIDE SURFACE
-0.02			275
-0.01			224
0	211	202	
0.01	279		214
0.05	237		
0.09	267		188
0.13	283		
0.17	292		201
0.21	284		
0.25	286		208
0.29	290		
0.33	277		207
0.37	290		
0.41	273		198
0.45	267		
0.49	239		207
0.53	252		
0.57	247		205
0.61	226		
0.65	252	192	221
0.67	302		193
0.75	285		183
0.83	250		210
0.91	295		242
0.99	263		212
1.07	176		185
1.15	201		202
1.23	187	183	203
1.24	204		
1.39	189	166	
1.59	178	185	
1.83	196	181	
2.07	188		

TABLE VI – 7 – HARDNESS MEASUREMENTS – BATTELLE
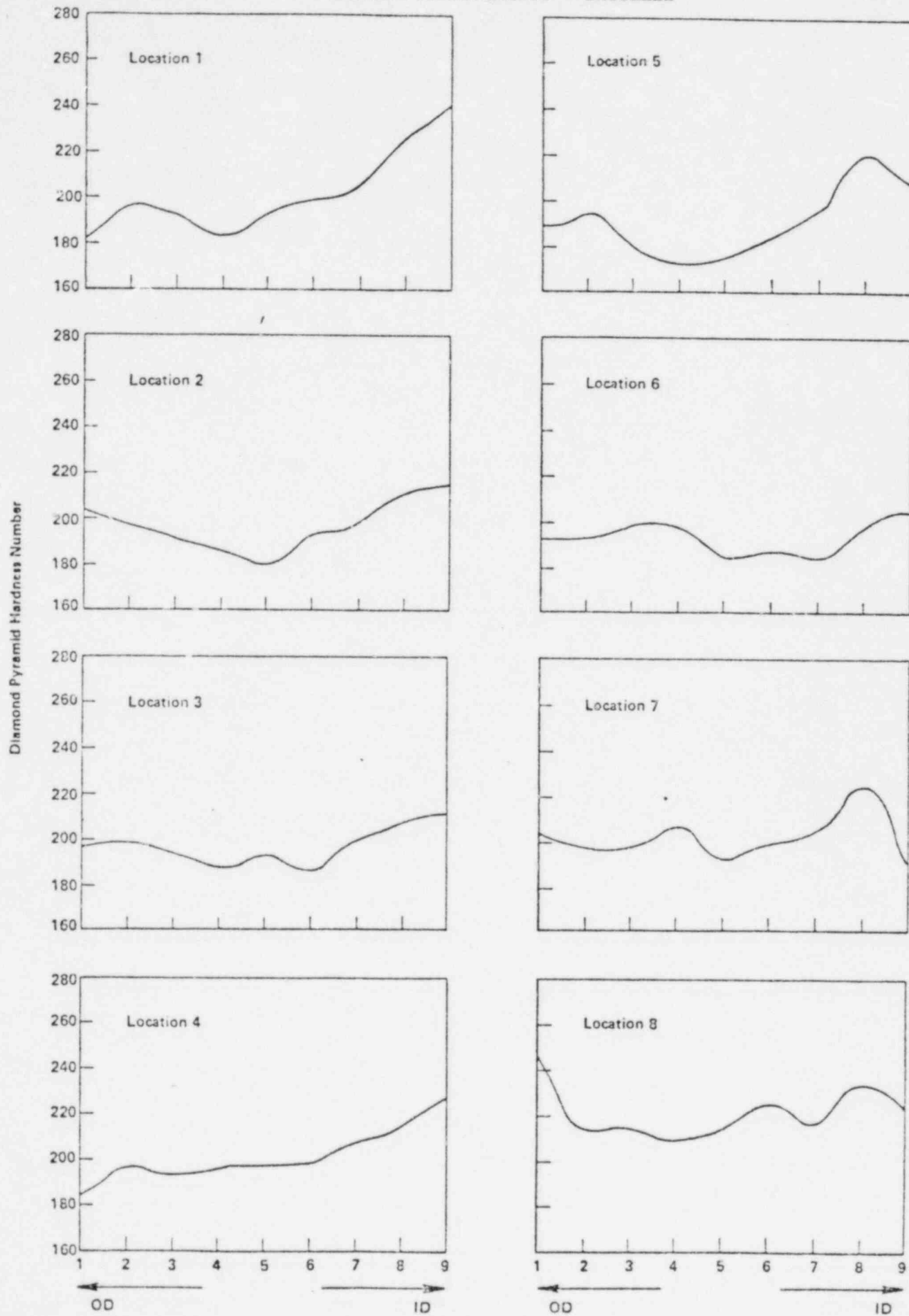
POSITION ACROSS THE TUBE WALL

TUBE A 146-8

TABLE VI – 7 (CONTINUED)
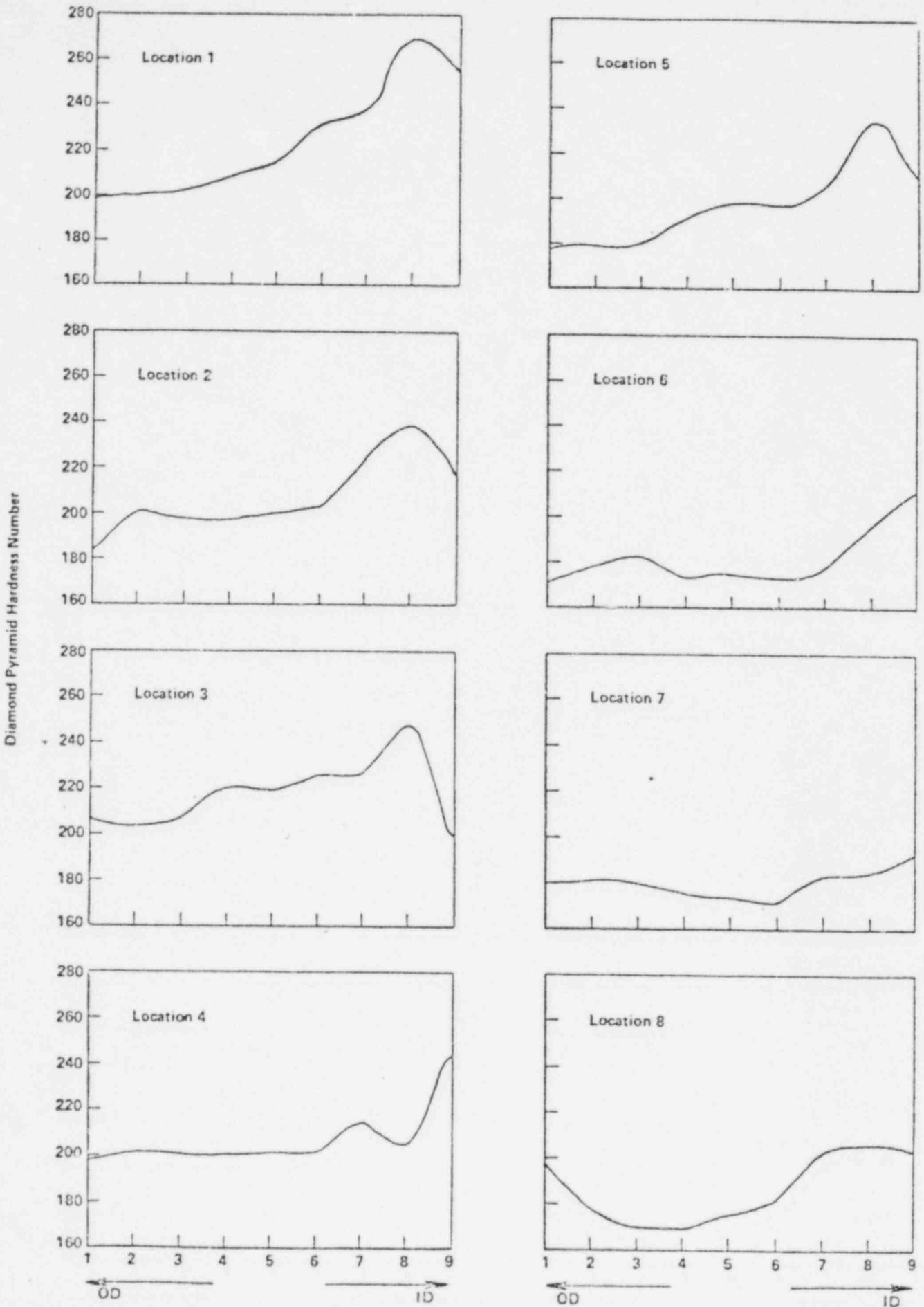
POSITION ACROSS THE TUBE WALL
TUBE A 146-6

TABLE VI - 8

WALL THICKNESS MEASUREMENTS

TUBE A-11-66

DISTANCE FROM TOP OF TUBE	WALL THICKNESS - INCHES
3/32"	.0367
7/32"	.0355
3/8"	.0355
1/2"	.0352
9/16"	.0350
5/8"	.0353
7/8"	.0366
1"	.0363
1-1/8"	.0363
1-1/4"	.0360
1-3/8"	.0363
1-7/8"	.0363

TABLE VI - 9

FAILURE ANALYSIS RESULTS

MECHANICAL TESTING

TUBE NO.	A-71-126	B-33-30	A-13-63[1]		ASTM
AXIAL LOCATION	60 7/16-68 11/16	33 1/4-41 3/4	2 5/16-10 7/16		B-163
HEAT NO.	M 1671	M 2867	M 2408		
T.S., PSI	101,000	101,000	44,500[2]	59,200[3]	80,000
Y.S., PSI	53,000 PSI	53,000 PSI	38,000[2]	50,000[3]	35,000
ELONG.		33%			30%

(1) Eddy Current Defect 90-100% TW at 7 1/8"

(2) Based on nominal cross section

(3) Based on actual cross section - 75% of nominal

TABLE VI - 10

CHEMISTRY DATA

Tube No. Heat No.	A-71-126 MI671			B-33-30 M2867		
	Analysis	Heat	Check	Analysis	Heat	Check
C	.034	.027	0.30	.041	.031	.033
Cr	15.3	14.94	15.53	15.66	15.15	15.22
Ni	74.38	74.66	73.47	74.90	76.35	76.22
Fe	9.6	9.30	9.80	7.76	7.37	7.40
Mn	.36	.30	.32	.40	.34	.34
S	<.01	.002	.0003	<.001	.0018	.0030
P	.01			.011		
Si		.33	.35	.35	.28	.29
Ti	.20	.19	.24	.28	.20	.21
N	.013			.013		
B		.0027	.003	.008	.0030	.0028
Co	.1	.01	.01	.075	.030	.030
Al	<.1	.13	.16		.17	.16
Mg					.019	.021
Cu	<.01	.01	.015		.03	.03
Mo	<.1					
Cb	<.1					

FIGURE VI - 1

SKETCH OF TYPICAL CRACK SHAPES
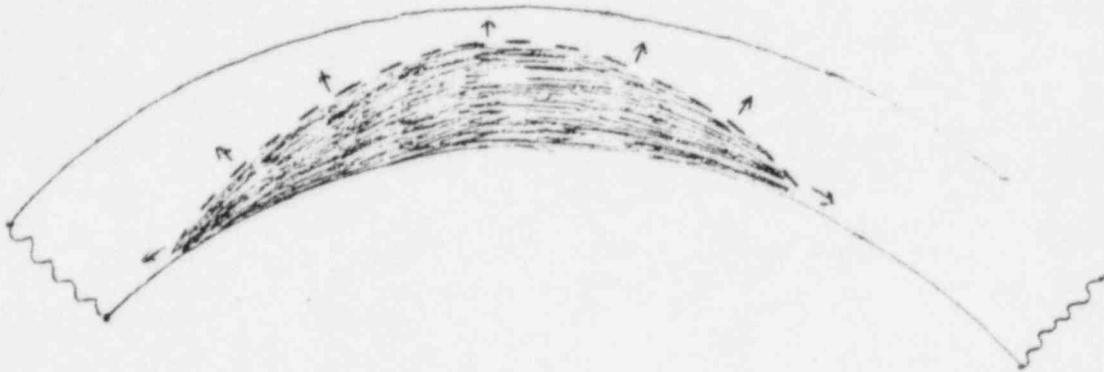
a) Advancing crack not yet through wall.

b) 100% through-wall crack continuing to grow.

FIGURE VI - 2
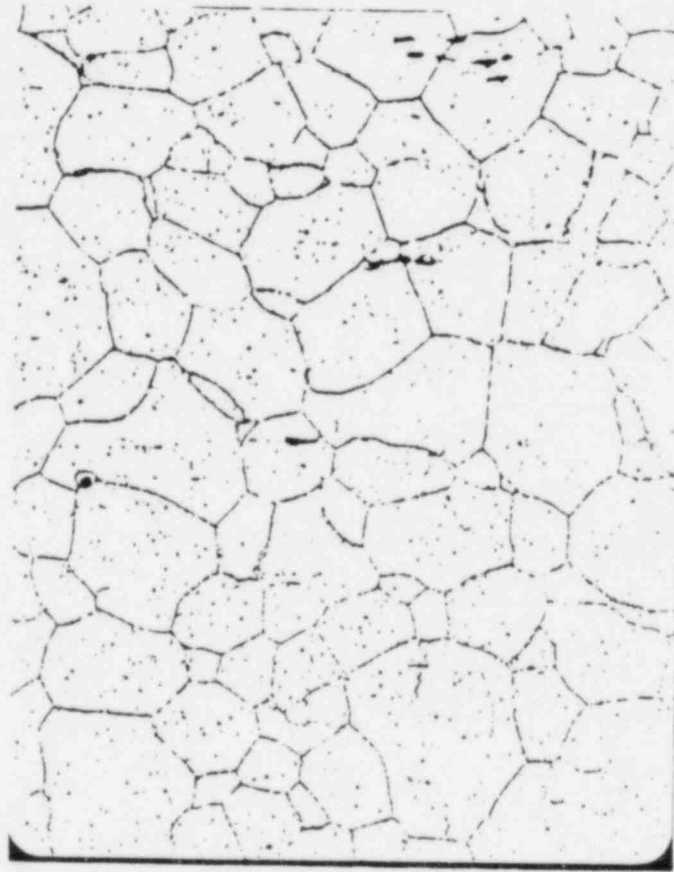
146-B   Top H_3PO_4 Etch

⑬   500X

FIGURE VI - 3

Atomic Percent Versus Position -
As Received

(X) 11-66
(⊙) 13-63
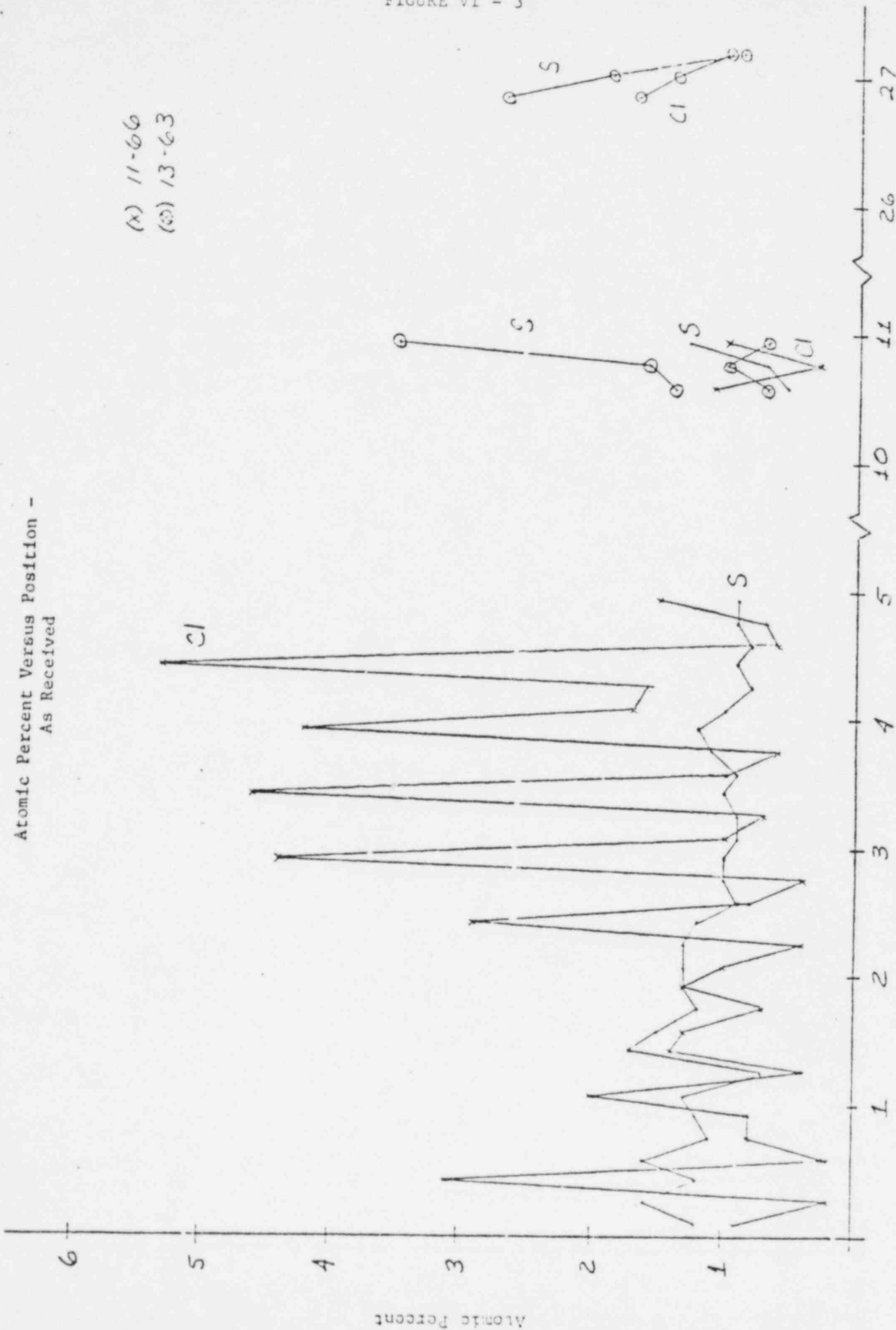
Distance From Top of Sample, Inches

Atomic Percent

PLASTIC STRAIN VS POSITION
TMI-1 TUBE SAMPLE A11-66
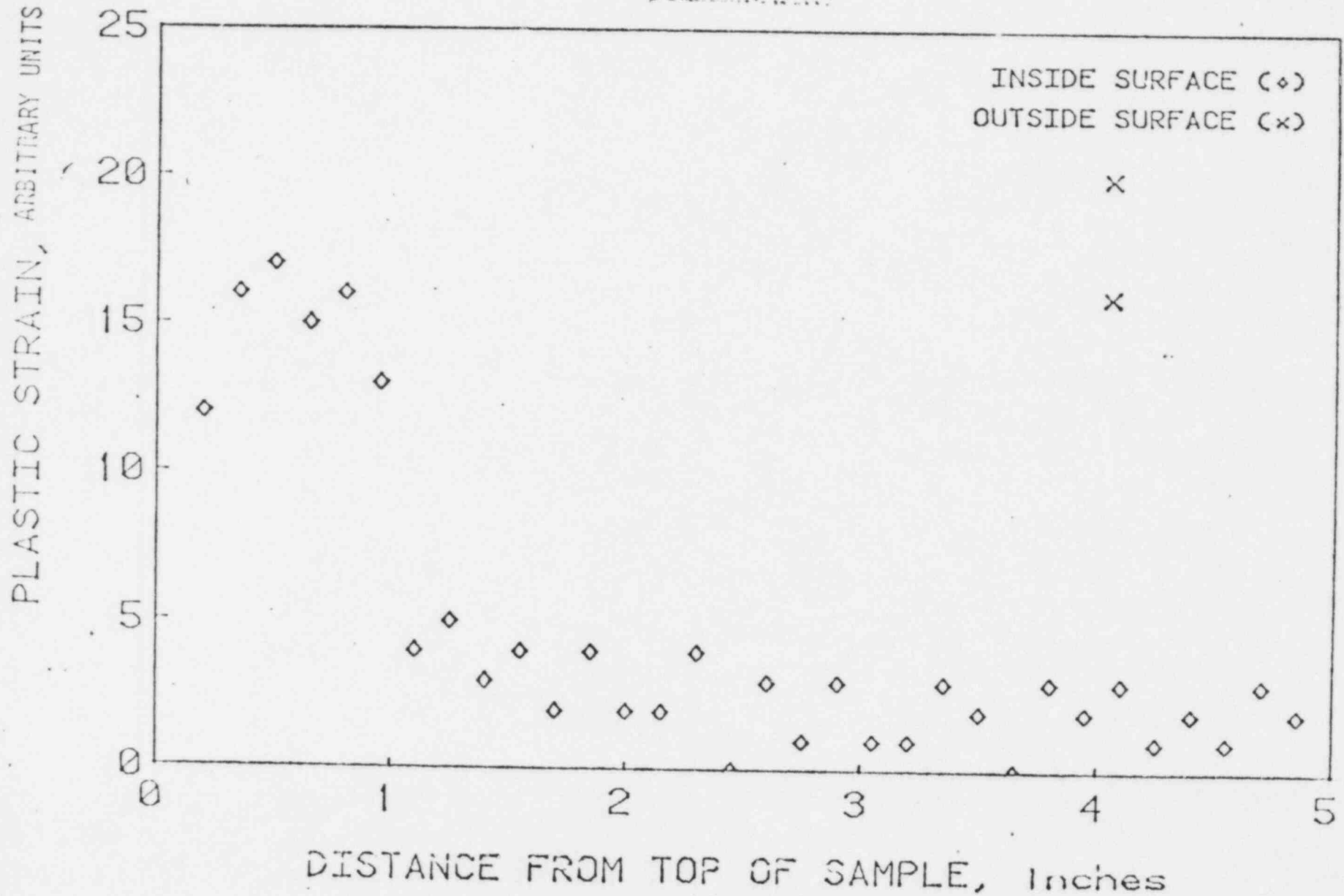
RESIDUAL STRESS VS POSITION
TMI-1 TUBE SAMPLE A11-66
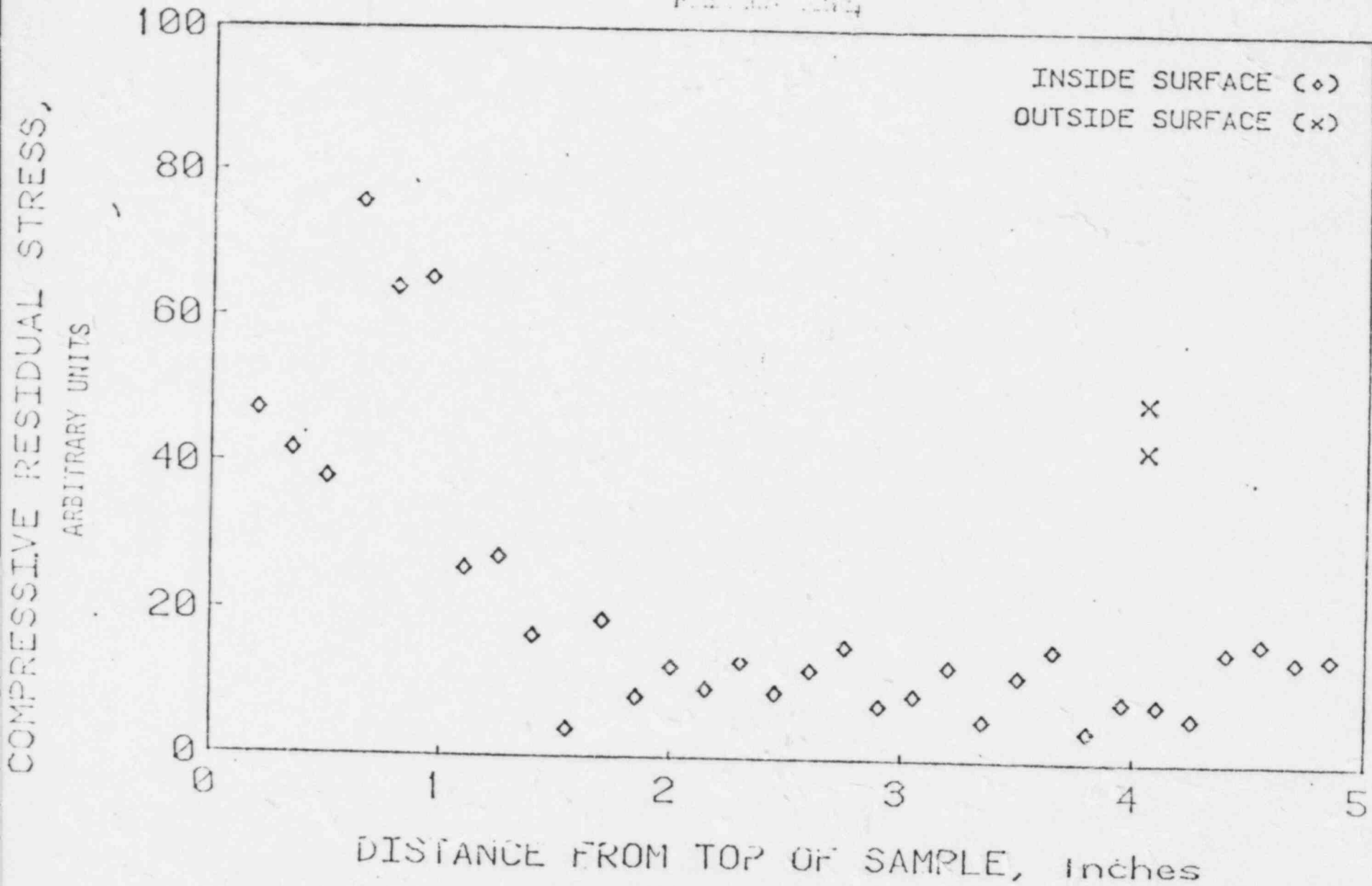
FIGURE VI - 5

VII.   TMI-1 OTSG FABRICATION HISTORY

A chronological listing of the following key events in the tube fabrication history is provided in Figure VII - 1.

° Tube Hollow Round Manufacturing
° Tube Making Process
° Tube Installation
° OTSG Stress Relief (Tubes Installed in Vessel)
° OTSG Site Storage

The detailed fabrication history is presented in reference 2.

A. Tube Raw Material Melting

The raw material for OTSG inconel tubing was melted by B&W - Tubular Products Division (TPD).*   Individual elements were first purchased from material suppliers (i.e., nickel, chrome, iron, etc.). Ordering specifications for these elements placed requirements for purity and limitations on undesirable trace elements. Proportional amounts of each element were electric arc melted. Spot checks of the molten metal were made and additional elements added as required to achieve the SB-163 Ni-Cr-Fe chemistry. The official ladle analysis was made just prior to pouring into ingots. A final check analysis was made of the ingot after cooling.

B. Hollow Rounds Fabrication

Hollow rounds fabrication was performed by B&W-TPD. Inconel ingots were first hot formed into blooms. The blooms were hot rolled into 8" diameter solid bars. A hot extending operation next formed 4" hollows from the bars. The 4" hollows were then cold worked to 2" O.D., .188" wall. The cold working operation was performed in two passes. An open fired annealing was performed after each cold working operation.

C. Tube Fabrication

All tubes used in the TMI-1 OTSG's were manufactured by Pacific Tube Company, Los Angeles, CA. Although PATCO has no records of the tubing supplied for the TMI-1 generators, interviews of PATCO personnel involved in the TMI-1 tube manufacturing process and review of B&W correspondence during this time period provided a relatively complete description.

The tube manufacturing facility at PATCO was designed around the order requirements for nuclear grade tubing.

*Organization name has subsequently been changed to Tubular Products Group (TPG).

Care was taken in the manufacturing of the tubes to prevent contam-
ination such as sulfur from coming in contact with tubes. All
handling of tubes was closely controlled (gloves were worn by
personnel and tube holding devices were made of Inconel). It was
noted that if any contaminants were on tubes during the drawing
process, the tubes would have a discoloration after final anneal-
ing. Tube discoloration was cause for rejection of a tube.

A brief description of the tube making process is provided below:

- tube hollows received by PATCO - 2" O.D., .188" wall

- tube hollow reduced to 1 1/4" O.D., .080" wall (rocker die - 1
  draw)

- cold drawing to .625" O.D., .034" wass (floating mandral - 4
  draws)

- bright annealed

- straighten (rotary-six roll straightener)

- centerless ground

An intermediate anneal was performed after each drawing operation
and tubes were cleaned prior to each annealing. Intermediate
anneals were performed in a bright annealing furnace at 1750°F.

The final tube annealing was performed in a two zone continuous
feed hydrogen furnace. The environment temperatures were 1800°F
for the first zone and 2000°F for the second zone. The tubes were
processed through the furnace at a rate of 50 inches/minute. Based
on the temperature of the furnace and the feed rate, actual tube
metal temperature was between 1950-2000°F.

Prior to shipment to B&W, the tubes received the following NED
tests: Ultrasonic Test, Liquid Penetrant Test, Eddy Current,
Hydrostatic Test and Metal Comparator Check.

D. Tube Installation

The OTSG Inconel tubes were received by B&W-NED (Barberton, Ohio)
from the PATCO individually wrapped in paper and packaged several
hundred to a lot in long wooden boxes. The boxes were loaded onto
tubing racks and elevated to the required height of area of tube
sheet being tubed.

All tube installation steps were performed with the generator in
the horizontal position with "Z" axis up. (See Figure VII-2.)
Normal tubing procedure was to begin at the top of the tubesheet
and thread tubes into the vessel in horizontal rows until tubing
was completed at bottom of the tubesheet. The tubing operation was
performed one tube at a time, except for the manway area, which was
the final area to be tubed utilizing a cluster of some 750 tubes.

During the tubing operation, the tubes were removed from a box one at a time, paper wrapping removed, handled with clean white cloth gloves, and immediately hand inserted into the vessel. During the actual insertion of each tube, each was wiped with an acetone wetted clean cloth and visually inspected. For the manway area, the tubes were also individually unwrapped, cleaned, inspected and placed into a tubing fixture, protected from damage and cleanliness maintained, and tubed as a group.

Following the completion of vessel tubing, all tubes at the lower tubesheet end were roller expanded into their respective tubesheet holes. The expanding operation itself was performed by shop personnel under direction of shop supervision. A written procedure was issued by Tool Design which described expanding operation to be followed and dictated periodic cleaning, roll replacement and inspection.

Once the tube ends were 100% expanded on the lower end of vessel, the tubes were pretensioned. This was accomplished by premeasuring tube ends on the upper end and air heating tubes to obtain required growth, thus obtaining pretension on cooling after rolling.

Using the same procedure as used in the lower end, the tubes were roller expanded in their respective upper tubesheet holes.

The tube to tubesheet welding was performed following roll expansion of the tubes by an automatic procedure. The welds were subsequently visually and dye penetrant inspected followed by helium and hydrostatic leak tests (hydrotest performed after post weld OTSG stress relief). Leaks at the tube to tubesheet weld discovered during the hydrotest were repaired by the following method:

° Remove portion of weld in area of leak

° Expand tube to 2 5/16" (maximum) depth overlapping original expanded area by 1/8"

° Dry-out tubesheet crevice area

° Re-weld area removed around tube leak

E. OTSG Stress Relief

The thermal cycle applied to the completed vessels was to perform the ASME Code post-weld heat treatment to all welds which had not previously received a stress relief. Welds either side of both tubesheets were in this category. B&W Engineering recognized the need for supplemental Code PWHT limits to protect the integrity of the vessels, therefore, a set of structural limitations were also imposed. The required Code cycle was to heat to 1100-1150°F, hold the welds requiring PWHT for a minimum of one hour per inch of thickness in the 1100-1150°F range, furnace cool to below 600°F. The maximum permitted ASME Code heating and cooling rates were 100°F/hour.

Due to the B&W imposed structural limitations, and the thermal attributes of the installed furnace power, furnace insulation, vessel mass, artificial cooling devices, etc., heating rates in excess of 20°F/hour were not achieved above 600°F, and cooling rates above 600°F were probably never greater than 15°F/hour. Also, because of structural limitations, controlled heating and cooling above 200°F was utilized.

Because of this slow process, Unit-1 (A-OTSG) took about 113 hours from start to beginning of cool, plus 134 hours of cooling to below 200°F. Unit-2 (B-OTSG) took about 84 hours from start to beginning of cool, plus 130 hours of cooling. Tubes on Unit-1 were above 1100°F (average of all tube temperatures) for 18 hours while Unit-2 tube average temperature was above 1100°F for 13 hours. The following is a brief description of the stress relief operation.

The furnace consisted of six lengthwise electric zones of approximately 14'2" each of 85' total, by 18' wide x 18" high. Heating elements were installed in the support car floor, the furnace roof and each end wall. One end wall was the furnace door. The vessel was set on the car to a prescribed location and oriented with "Z" axis down rotated 12° clockwise off of the major axis (See Figure VII-3).

Stainless steel duct piping was welded to the top vessel nozzle, one bottom nozzle and to two secondary side openings. These connections were flow loops which were installed outside the furnace proper, in the adjacent equipment room. Each flow loop consisted of one or two axial flow fans, an electric heater and a cooler. Each loop was built to be evacuated after welding the vessel into them, and backfilled with argon gas.

Prior to the above steps of vessel loading and connection to the ducts, numerous sheath thermocouples were placed in the tubes at prescribed locations and on the I.D. surface of the primary welds (heads to tubesheets). Thermocouples were installed at prescribed locations on the vessel O.D. also.

Extensive care was taken to assure that all thermocouples were connected to a prescribed, pre-assigned recorder or controller channel. Data sheets were designed to be filled out hourly. The data was reviewed and reduced to pertinent summary conditions to compare with the permitted structural limitations.

The entire operation was largely manual in many respects, regardless of the use of the automatic program controllers, as many manual operations were required due to the hourly reviews of the process status. Heating rates on the order of 20°F/hour at the beginning but as low as 5°F/hour near hold range were common.

In general cooling rates of no more than 15°F/hour were used. Actual metal temperature changes probably did not exceed 20°F/hour over extended lengths of time. Overall cooling rates (1100°F to 200°F) were on the order of 7°F/hour for the TMI-1 units.

Plots of Unit-1 and 2 post-weld heat treatment (average) shell/tube themocouple readings are provided in Figure VII-4. These plots depict the gradual heatup and cooldown ramps above 200°F. The close tie between tube and shell temperature over the entire range is also identified.

A detailed review of individual hourly thermocouple readings indicates tube temperatures varied less than 40°F radially across the upper tubesheets. This data also indicates the highest themocouple readings were located at the center of the tube bundle during heatup and at the outer tubes near the "X" axis during cooldown. The lowest individual thermocouple reading varied at different locations on the outmost tubes during the entire cycle.

It is common B&W practice to obtain surface samples of the OTSG secondary side tubes after all manufacturing operations are completed. One of the elements evaluated in these samples is sulfur. The TMI-1 units were found to have an average sulfur level of 162 and 216 ugms/ft^2 on the A and B tube surfaces, respectively. This compares to an observed range for other operating plants of 42-557 ugms/ft^2.

F. OTSG Shipping/Site Storage

The steam generators were transported to the site with shipping covers over all openings and desiccant for humidity control. At the site the vessels were stored outside with a nitrogen purge on the primary and secondary side. The above outside storage lasted one year to 18 months. At the end of this time period the vessels were moved into the containment building and upended. The exact method of storage for the following 2 1/2 years before commercial operation is not readily available and not a subject of this report.

G. Conclusions

The review of the TMI-1 OTSG tubing records indicate that acceptable engineering practices and manufacturing techniques were used throughout the manufacturing process. Furthermore, no fabrication information has been found which can be related to the tube eddy current defect patterns as noted in the A and B-OTSG.
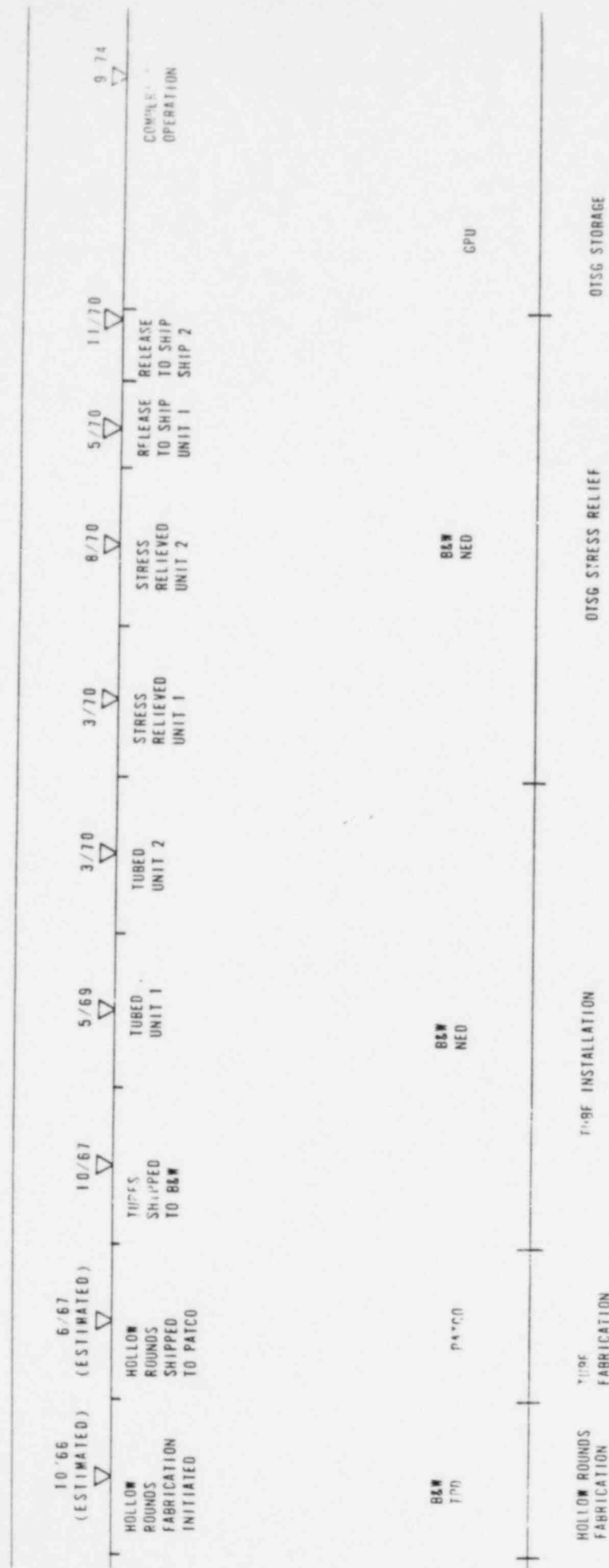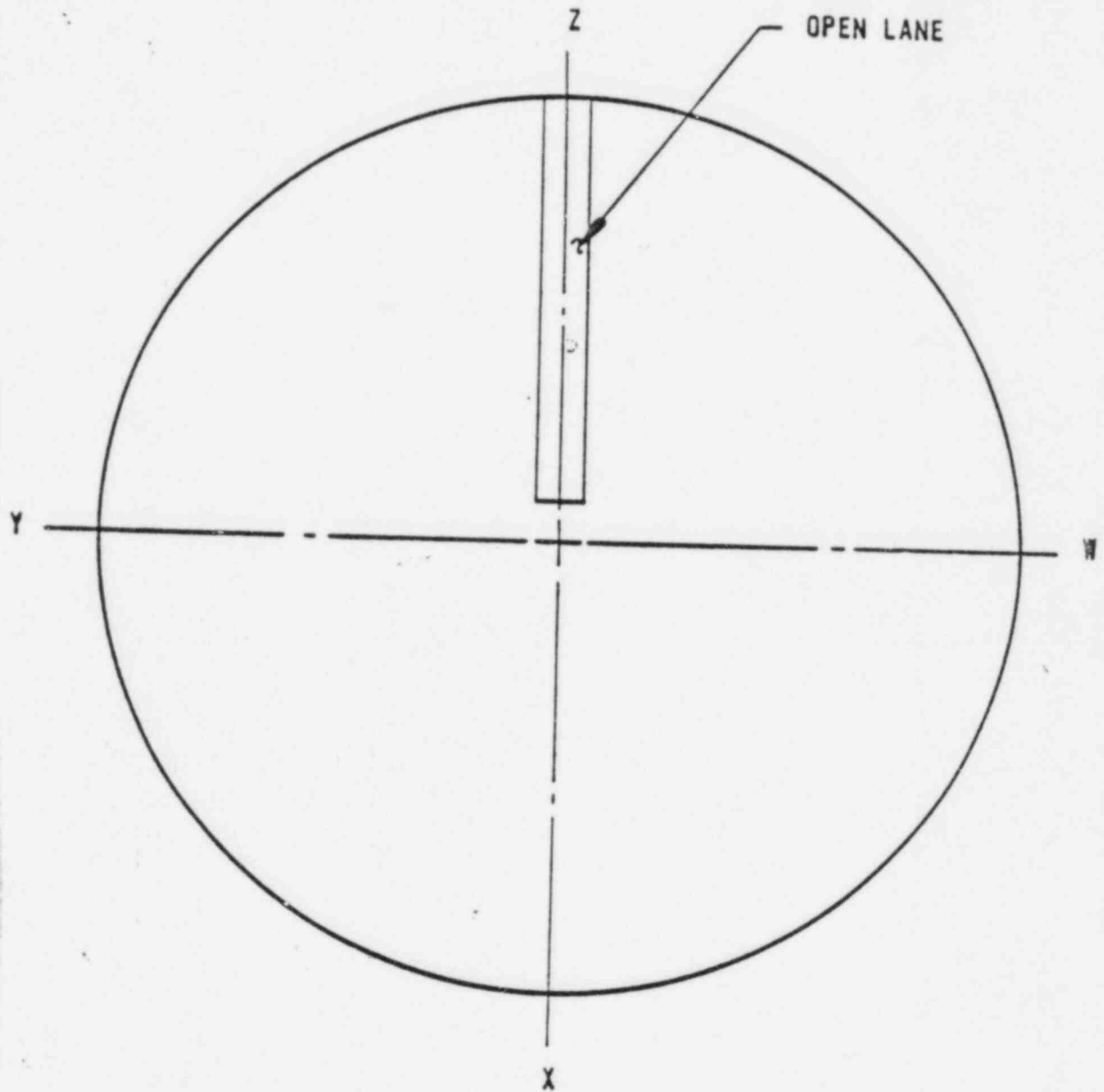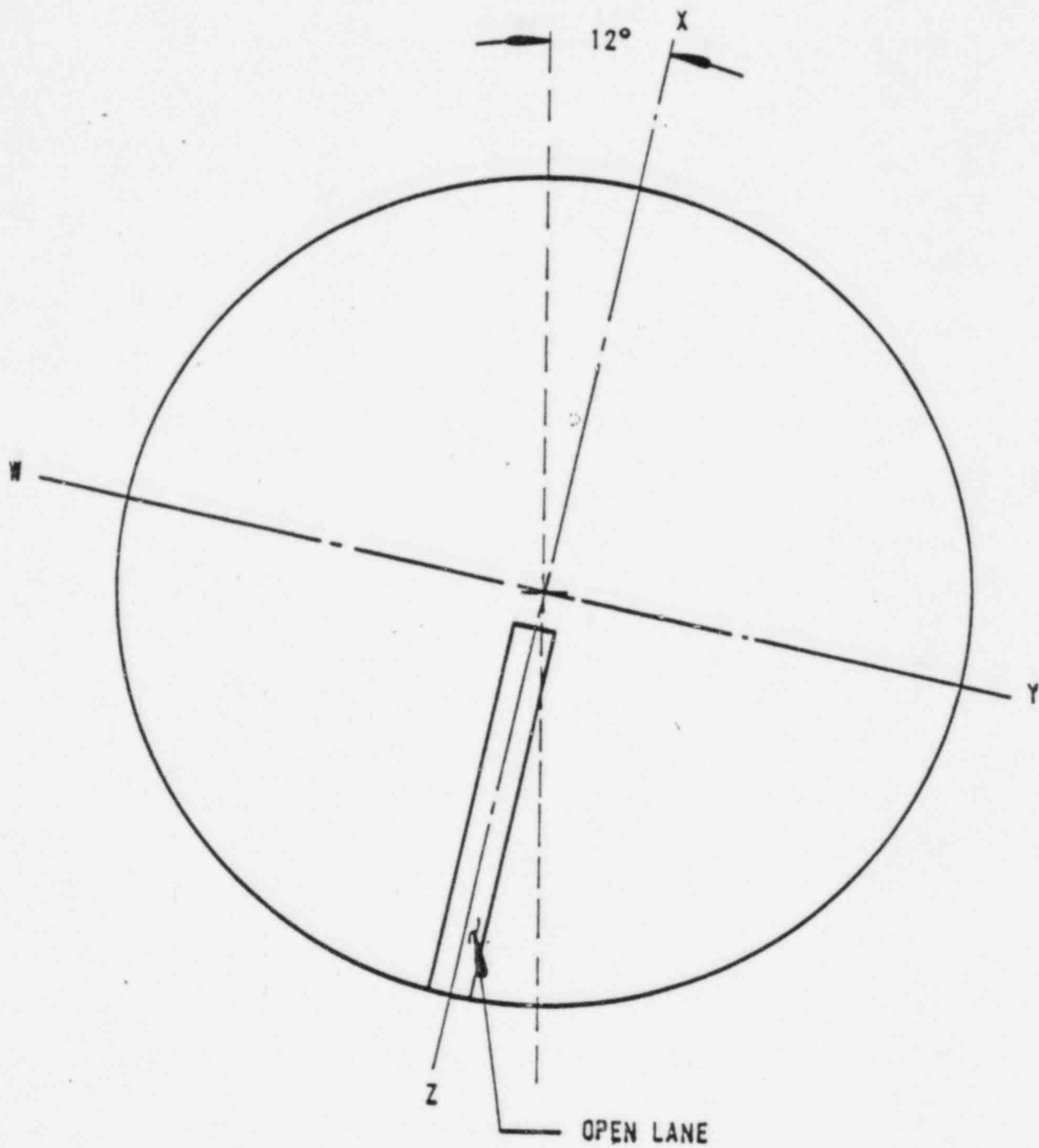
TMI-1 OTSG TUBE HISTORY OVERVIEW

10/66 (ESTIMATED)	6/67 (ESTIMATED)	10/67	5/69	3/70	3/70	8/70	5/70	11/70	9/74

HOLLOW ROUNDS FABRICATION INITIATED

HOLLOW ROUNDS SHIPPED TO PATCO

TUBES SHIPPED TO B&W

TUBED UNIT 1

TUBED UNIT 2

STRESS RELIEVED UNIT 1

STRESS RELIEVED UNIT 2

RELEASE TO SHIP UNIT 1

RELEASE TO SHIP UNIT 2

COMPLETE OPERATION

B&W TDD

PATCO

B&W NED

B&W NED

GPU

HOLLOW ROUNDS FABRICATION

TUBE FABRICATION

TUBE INSTALLATION

OTSG STRESS RELIEF

OTSG STORAGE

FIGURE VII-1

FIGURE VII-2

ORIENTATION OF GENERATORS DURING TUBING OPERATION

FIGURE VII-3

ORIENTATION OF GENERATOR DURING POST WELD STRESS RELIEF

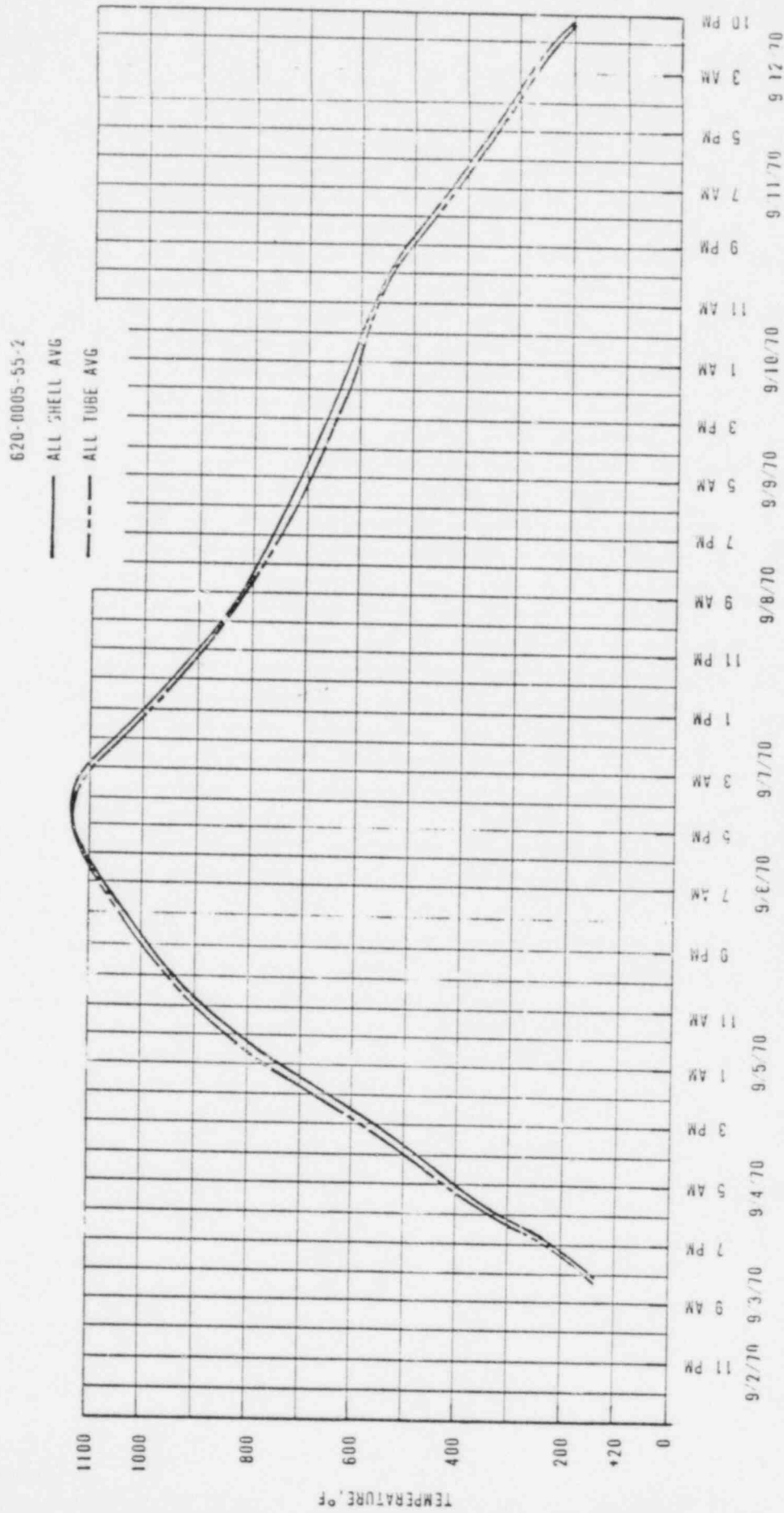FINAL FUEL VESSEL PWHT IN OTSG ELECTRIC FURNACE IN BARBERTON

FIGURE VII-4
sheet 1

620-0005-55-1

------ ALL SHELL AVG

—·—· ALL TUBE AVG

TEMPERATURE, °F

1100
1000
800
600
400
200
420

TIME

3/2/70 3/3/70   3/4/70   3/5/70   3/6/70   3/7/70   3/8/70   3/9/70   3/10/70   3/11/70   3/12/70

5PM 3AM 1PM 11PM 9AM 7PM 5AM 3PM 1AM 11AM 9PM 7AM 5PM 3AM 1PM 11PM 9AM 7PM 5AM 3PM 1AM 11AM 9PM 7AM 5PM 11PM
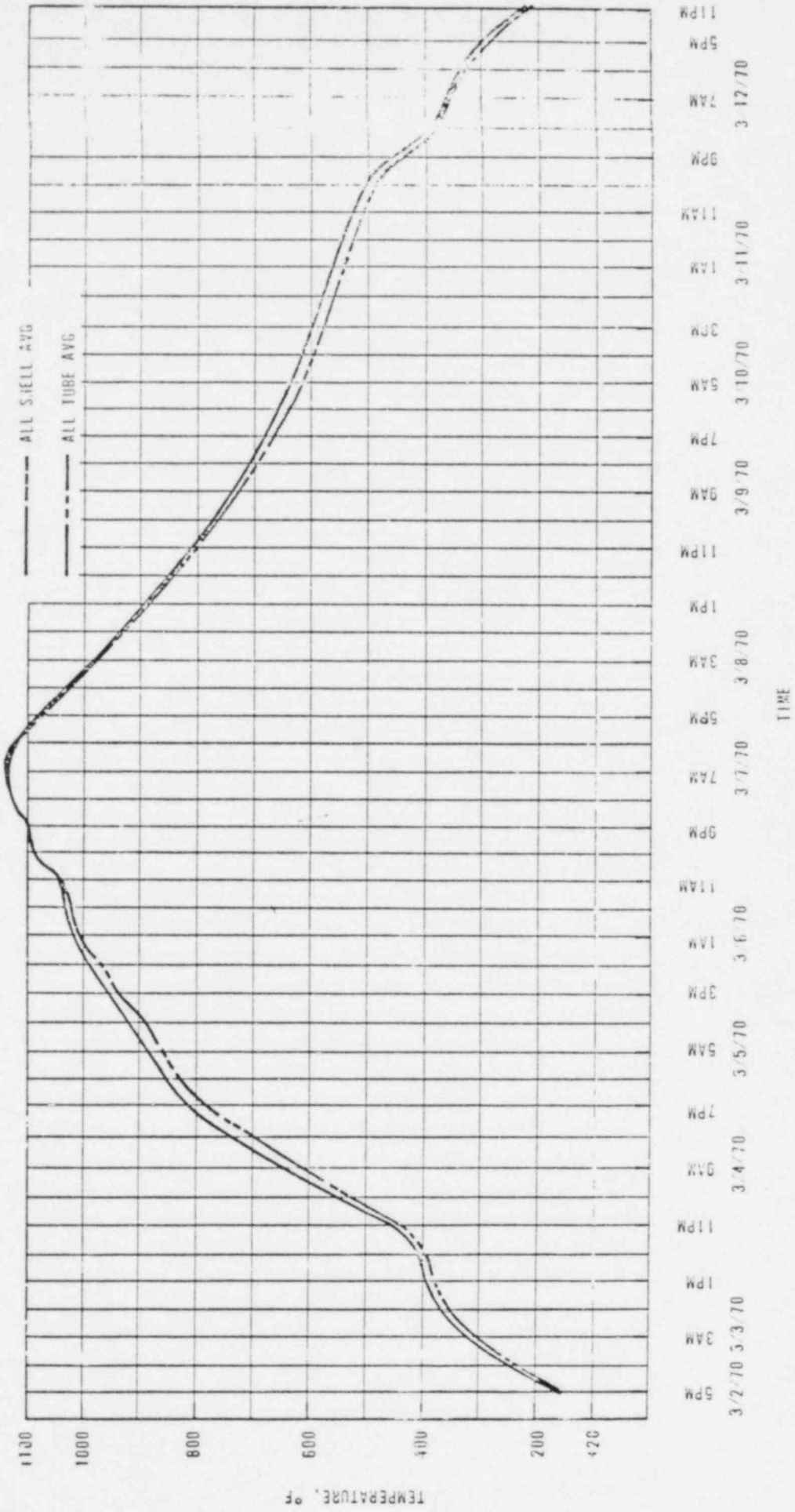
FINAL FULL VESSEL PWHT IN OTSG ELECTRIC FURNANCE IN BARBERTON

FIGURE VII-4
sheet 2

620-0005-55-2

——— ALL SHELL AVG
– – – ALL TUBE AVG

VIII. <u>OTSG TUBE STRESS ANALYSIS</u>

A. Introduction

Intergranular stress cracking defects originating at the tube inside diameter and oriented circumferentially have been found on a substantial number of the TMI-1 steam generator tubes. The cracking distribution has been divided for analysis into four locations: the heat affected zone of the seal weld, the roll, the roll transition, and the free standing tube. Accordingly, stresses (residual and applied), in particular, axial tensile stresses have been estimated and computed at these four locations to determine how well these stresses can be correlated with the actual defects found.

B. Stress Calculation Results (See Reference 3 for more details)

1. Residual Stress

Table VIII-1 shows best estimate residual tensile stresses (including those due to tube preload) at the inside diameter of the tube for the steam generators as now installed at TMI-1.

Figure VIII-1 shows the tube/tubesheet joint configuration at TMI-1 and our estimate of the residual stress distribution in this joint. Figure VIII-2 shows a plot of the tube wall thicknesses as measured from an actual tube sample removed from one of the TMI-1 steam generators. This figure indicates that there was a roll transition (between rolled and unrolled portions of the tube) above as well as below the rolled joint. Accordingly, substantial axial tensile stresses are expected (due to rolling) above as well as below the roll area of the tube.

Figures VIII-3 and VIII-4, which are from a Huntington Alloys Technical Bulletin for Inconel 600 show that residual stresses remaining after 1150°F heat treatment reduce to above 22,000 psi. These figures, which are for cold-drawn 20% and cold-drawn annealed rod, are considered to be reasonably representative of the Inconel 600 tubes at TMI-1 since the tubes also had some cold work in the areas of interest.

The maximum stresses in Table VIII-1 exceed the 22,000 psi value by 4,000 psi which is our best estimate value for tube preload after the 1150°F heat treatment of the steam generators. The 4,000 psi preload stress value was calculated based on a 1981 fiber optics inspection, which showed tube B-22-30 at TMI-1 to be parted and separated by about 0.09 inches. Because of differential thermal expansion (tubes expand slightly greater than shell) between the tubes and the shell of steam generator when the steam generator was at 1150°F during heat treatment, this 4,000 psi stress was not subject to stress relief. Therefore, the 4,000 psi value was added in Table VIII-1 to the pertinent 22,000 psi residual stresses mentioned above.

It should be noted that the stresses in Table VIII-1 are sub-
stantially in excess of the stresses reported by EPRI by their
February 24, 1982 letter to GPUN. EPRI reported stresses between
20,000 and 5,000 psi for an 1150°F for 10 hours heat treatment.

2.   Applied Load Stresses

As indicated in other sections of this report, the intergranular
stress cracking found at TMI-1 probably occurred during the time
period following the cooldown transient of September 6, 1981.
Accordingly, the applied load stresses for the cooldown transient
discussed below may not have existed while the intergranular stress
cracking was occurring. However, there is a possibility that these
or other stresses from loads applied in the past still existed in
some parts of the tube/tubesheet joints.

Specifically, we consider it reasonable that applied loads may
have resulted in locked up axial stresses in both the rolled
portion of the tube and in the weld HAZ of the tube. For this
condition to have existed, it is only necessary that some very
small amount of sliding occur between the tube and the tubesheet in
the rolled joint. If the load capability of the rolled joint were
about equal to an applied load, then some sliding could occur. If
the applied load were then removed and no sliding to the original
position occurred, then axial tensile stresses would be locked into
the tube within the roll and weld HAZ regions.

Accordingly, we conclude that applied load stresses may have been a
contributor to the intergranular stress cracking at TMI-1 and our
best estimate values for the September 6, 1981 cooldown transient
are presented in Table VIII-2. See Figure VIII-5 which pertains to
this cooldown transient.

The axial stress values in Table VIII-2 are about half those for a
design basis cooldown. As can be seen from Figure VIII-5, the
September 6, 1981 cooldown was relatively gentle regarding tube
loads even though some short step changes in temperature did
occur. Tube loading due to this transient is mainly proportional
to the maximum mismatch in temperature (90°F) between the steam
generator shell and the tubes; also, pressures in the steam gener-
ator have some effect.

The applied load stresses agree reasonably well with those devel-
oped by EPRI in their Report NP-2146, which was based on TMI-2 tube
loads measured by strain gages. Specifically, a maximum axial load
stress of 10,185 psi was calculated for a tube near the periphery
during a cooldown transient which was more severe than

the September 6, 1981 transient at TMI-1. This 10,185 psi EPRI
value compares favorably with the 11,000 psi value in Table
VIII-2.

The axial stresses in Table VIII-2 are noted to be higher in the
peripheral tubes than in the center tubes of the tube bundle. This
is calculated to occur primarily as a result of elastic deformation
of the tubesheets.

3. Conclusions

Table VIII-3 summarizes the combined maximum residual, preload and
applied stresses which are estimated to have occurred in the tubes
at both top and bottom tubesheets at TMI-1 on September 6, 1981.
Based on these stresses, we would conclude the following:

a. Stresses in the outer tubes are slightly higher than in the
    center bundle tubes. This is generally consistent with the
    actual defect radial distribution found at TMI-1.

b. Substantial tensile stresses are considered to have probably
    been present in the four locations where defects have been
    found axially within the tubes as indicated in Table VIII-3.

c. The stresses discussed herein are applicable to both the upper
    and lower tubesheets because the weight of a tube results in a
    negligible difference in stress for the bottom versus the top
    tubesheet. This and the fact that no substantial defects have
    been found in the lower tubesheet area indicate that some
    factor other than stresses has played an important role in the
    cracking of the tubes at the upper tubesheet.

TABLE VIII-1

TUBE RESIDUAL TENSILE STRESSES$^{(1)}$ PSI
AT FOUR LOCATIONS OF INTEREST

Location	Axial	Circumferential
Weld HAZ	22,000	-22,000
Roll	-10,000	-22,000
Roll Transition	26,000$^{(2)}$	22,000
Tube (between tubesheets)	0 to 26,000$^{(2),(3)}$	0 to 22,000$^{(3)}$

NOTES

(1) The stresses in this table are for the case where the rolled joint is
     tightly constrained by the tubesheet. If the rolled tube were loose in
     the tubesheet then circumferential stress in the loose roll area would
     approach zero and axial stress in the loose roll area would aproach
     about 4,000 psi. Axial stress in the weld HAZ would approach
     26,000 psi.

(2) This stress includes 4,000 psi due to tube preload after heat treat-
     ment. Such preload stresses are expected to be higher for the periphery
     of the tube bundle than for tubes located in the center of the bundle.

(3) Tube stresses between tubesheets are primarily due to the tube straight-
     ening manufacturing process and may vary considerably depending on the
     location within the tube.

TABLE VIII-2

MAXIMUM APPLIED LOAD TUBE STRESSES (psi)
FOR THE SEPTEMBER 6, 1981 COOLDOWN TRANSIENT

Location	Axial [2]		Circumferential[3]
	Center Tube	Outer Tube	
Weld HAZ	0 to 6,000	0 to 11,000	10,000
Roll[1]	0 to 6,000	0 to 11,000	0
Roll Transition	6,000	11,000	10,000
Tube (between tube-sheets)	6,000	11,000	10,000

NOTES

(1) The axial stresses in these locations can range from zero to the maximum values indicated depending on the actual tightness of the rolled joint.

(2) Axial stresses for outer bundle tubes are higher than for center bundle tubes because of the elastic deflection of the tubesheets. Tube preload stresses are not included in this table.

(3) These values are estimated stresses due to pressure loads, accurate values can be calculated, if the detailed configuration of the joint can be determined.

TABLE VIII-3

SUMMARY OF MAXIMUM ESTIMATED STRESSES CONSIDERING
MAXIMUM APPLIED DURING SEPTEMBER 6, 1981 COOLDOWN,
PRELOAD AND RESIDUAL STRESSES (psi)

Location	Axial [1]		Circumferential
	Center Tube	Outer Tube	
Weld HAZ	31,000	39,000	-12,000
Roll [2]	9,000	17,000	-22,000
Roll Transition	31,000	39,000	32,000
Tube (between tube-sheets) [3]	5,000 to 31,000	13,000 to 39,000	10,000 to 32,000

NOTES

(1) Axial stresses include estimated preload stresses of 3,000 psi for a center tube and 6,000 psi for an outer tube because of elasticity of the tubesheets.

(2) Axial stresses in the roll area are based on the assumption that the initial residual compressive stresses have been relieved and changed to tensile stresses due to preload and applied loads as a result of some sliding of the rolled joint.

(3) Tube stresses between tubesheets are primarily due to the tube straightening manufacturing process and may vary considerably depending on the location within the tube.
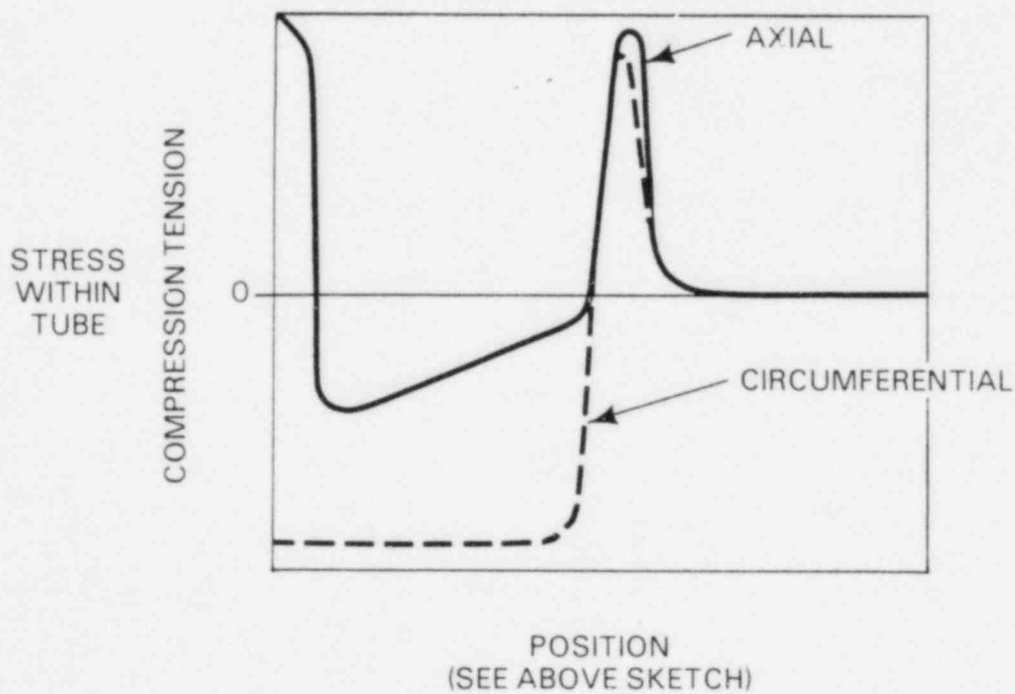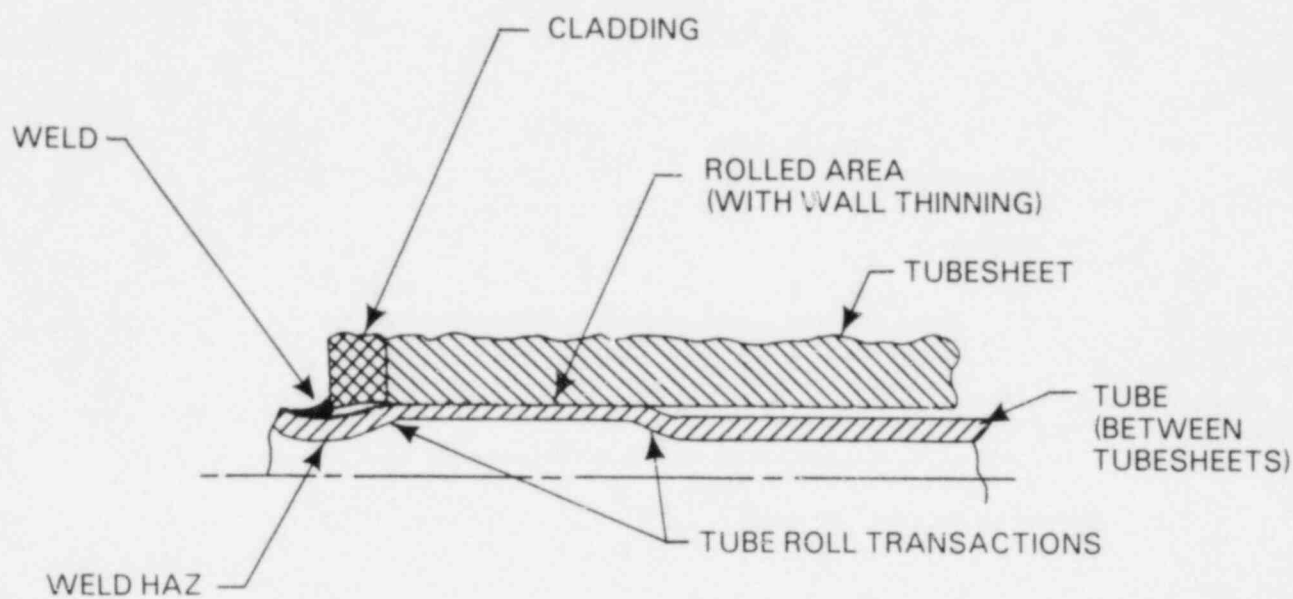
TUBE/TUBESHEET ROLLED/WELDED JOINT
ESTIMATED DISTRIBUTION OF TUBE RESIDUAL STRESSES
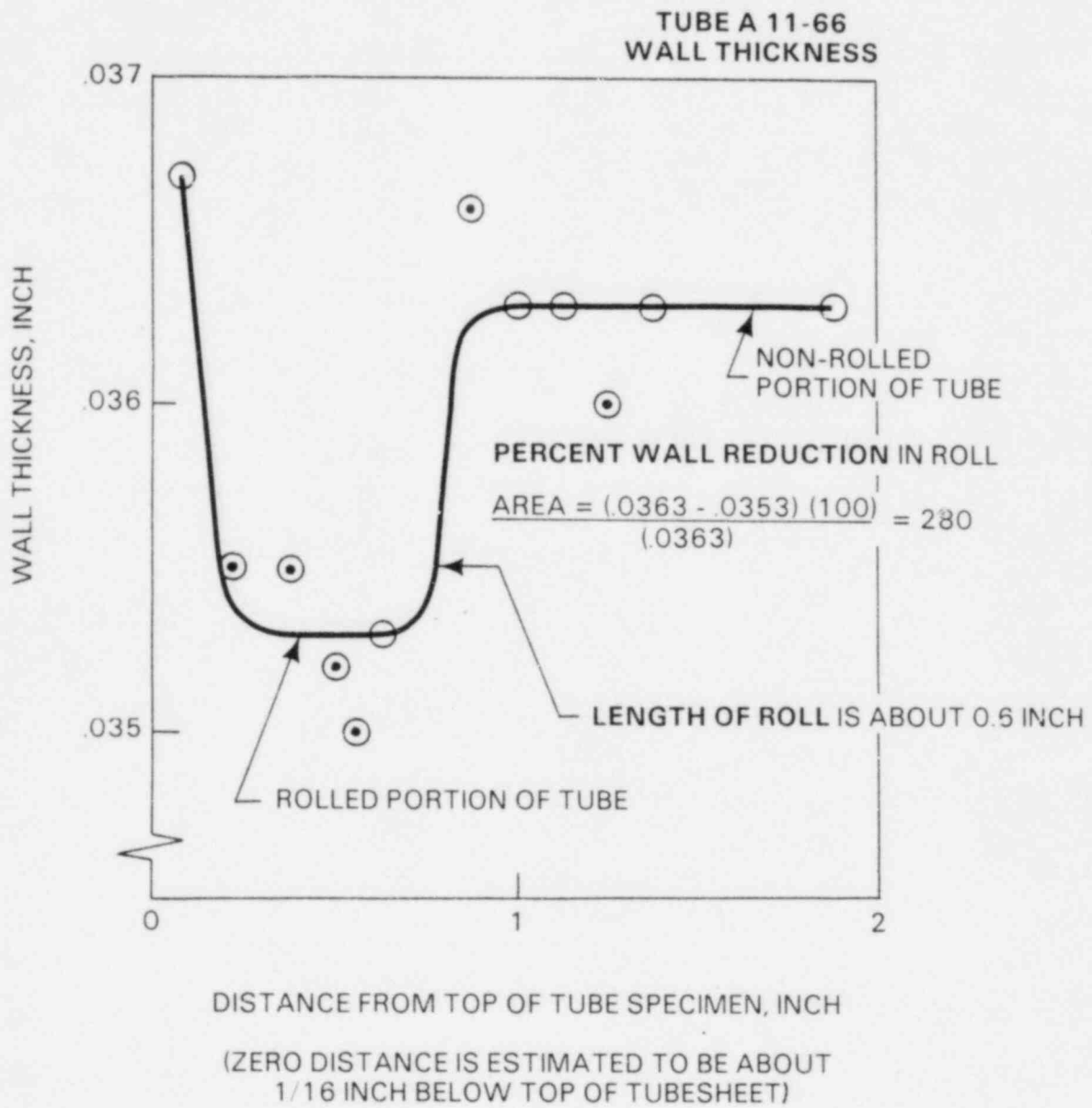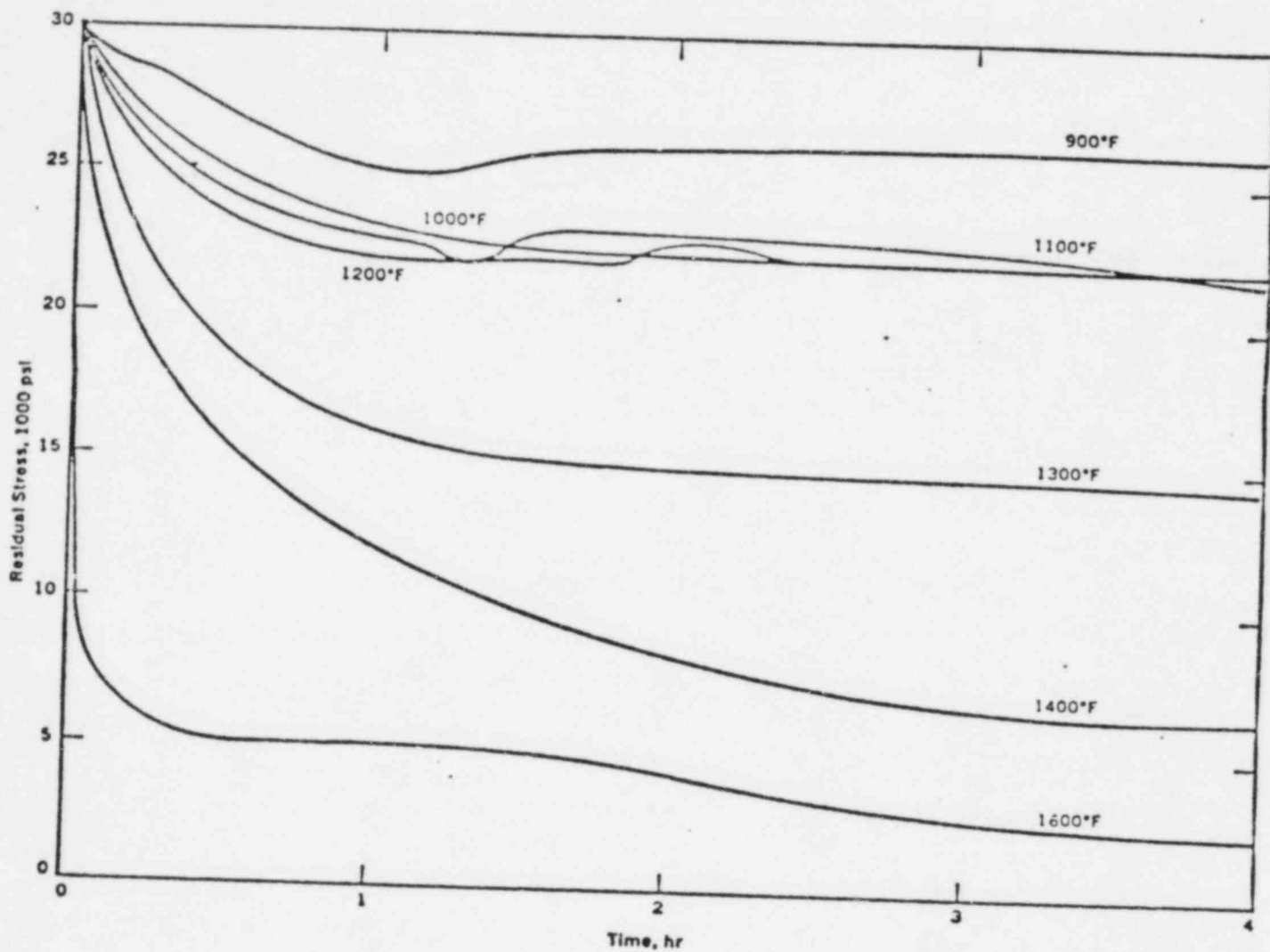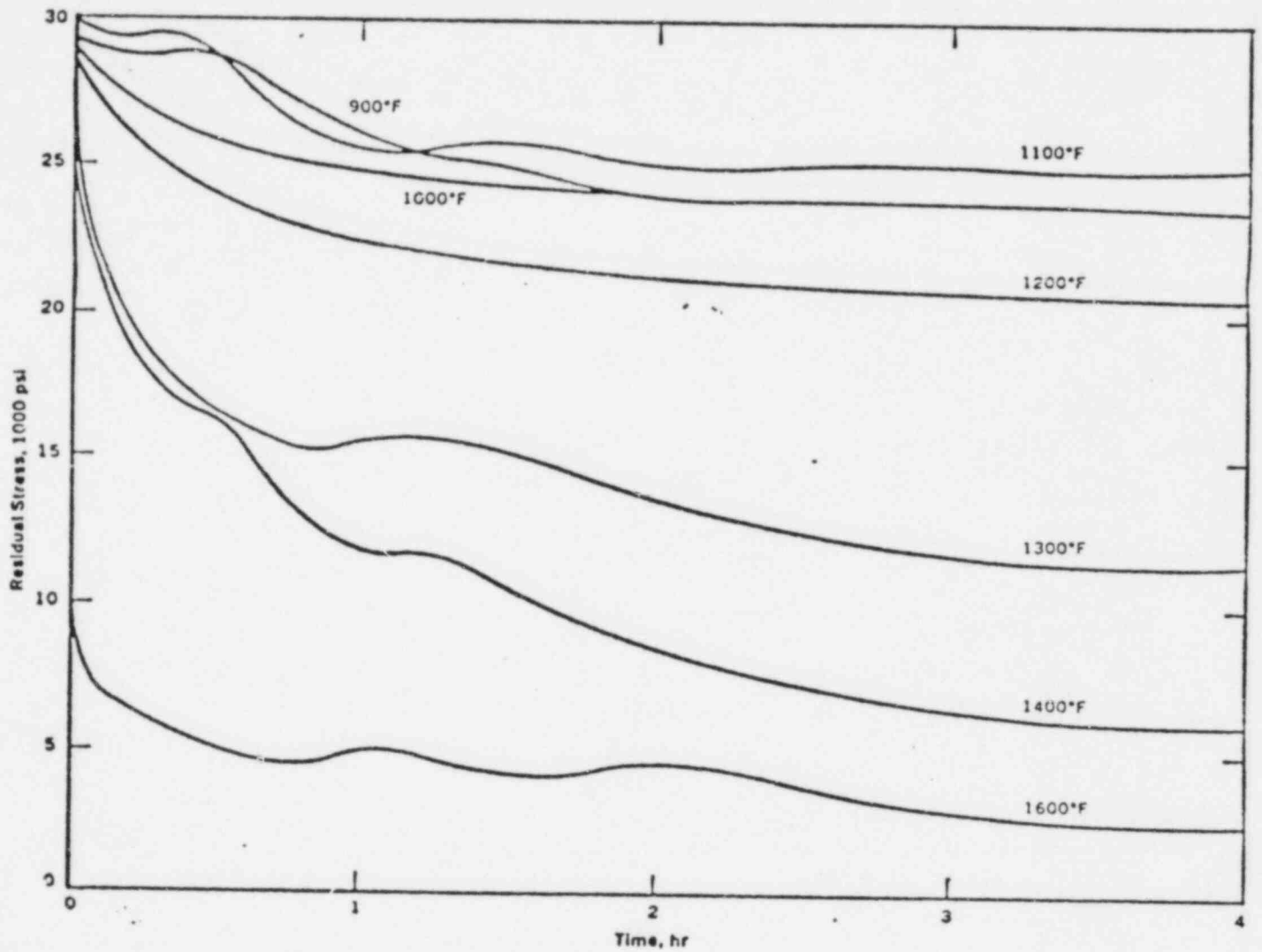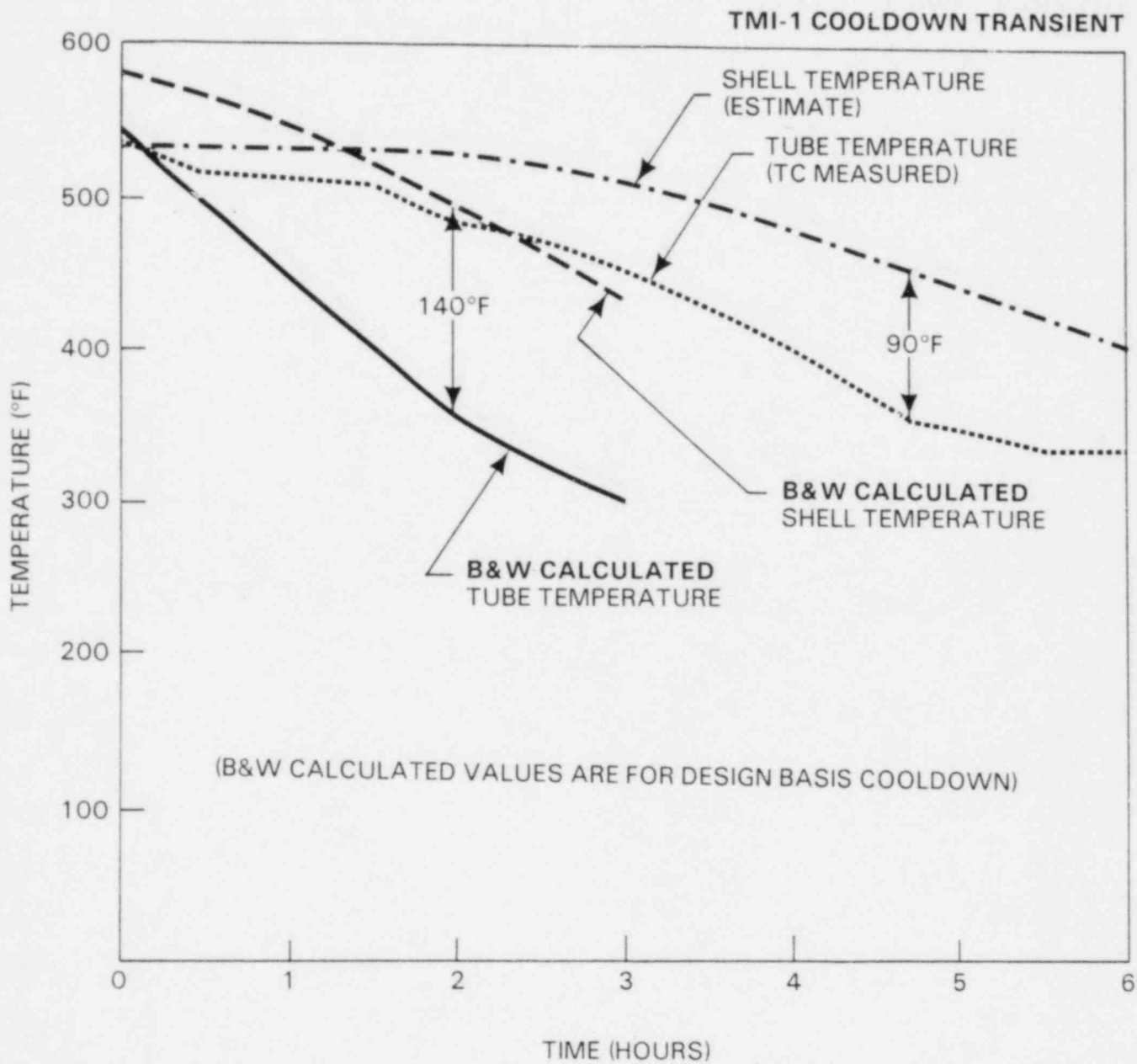
FIGURE VIII-1

TUBE A 11-66
WALL THICKNESS

WALL THICKNESS, INCH

NON-ROLLED
PORTION OF TUBE

PERCENT WALL REDUCTION IN ROLL

$$\text{AREA} = \frac{(.0363 - .0353)(100)}{(.0363)} = 280$$

LENGTH OF ROLL IS ABOUT 0.6 INCH

ROLLED PORTION OF TUBE

DISTANCE FROM TOP OF TUBE SPECIMEN, INCH

(ZERO DISTANCE IS ESTIMATED TO BE ABOUT
1/16 INCH BELOW TOP OF TUBESHEET)

FIGURE VIII- 2

EFFECT OF HEATING TIME AND
TEMPERATURE ON RESIDUAL STRESS OF
COLD-DRAWN (20%) ROD

FIGURE VIII-3

EFFECT OF HEATING TIME AND
TEMPERATURE ON RESIDUAL STRESS OF
COLD-DRAWN, ANNEALED ROD

FIGURE VIII-4

TMI-1 STEAM GENERATOR TEMPERATURES
DURING COOLDOWN TRANSIENT OF 9/6/81

FIGURE VIII-5

IX. CRACKING TESTING

A. Test Program

A cracking testing program has been developed and tests are underway at the B&W Alliance Research Center, Alliance, OH, Oak Ridge National Laboratories and Battelle Columbus Laboratories. The programs consist of five phases: 1) reproduce intergranular attack (IGA) in primary water environments, 2) arrest the attack, 3) verify the cracking scenario, 4) determine that the attack will not restart upon plant start-up, and 5) assess effect of tube repair techniques on material resistance to IGA. Results from this test program will be recorded in a separate report, Reference 11.

1. Reproduce IGA

a. Purpose

The purpose is to produce IGA in OTSG tubing in primary water and contaminated primary water, thus identifying the probable causative chemical(s).

b. Test Material

The test material is Alloy 600 OTSC tubing with a heat treatment equivalent to TMI-1 (i.e. mill annealed plus 1150°F/18 hours). Some tests will also be done with solution annealed plus stress relieved and actual TMI-1 tubing.

c. Test Specimens

Test specimens are stressed longitudinal strips of tubing. Unstressed rings of tubing.

d. Test Methods

Electrochemical corrosion tests are being used to screen test environments until causative environments are identified. Conventional exposure tests are being used to verify results obtained from the accelerated electrochemical corrosion tests.

e. Test

1. Baseline Boric Acid Environments 5000 H_3BO_3, 13,000 ppm H_3BO_3

2. Thiosulfate Contamination
   a) Borated water + 100, 10, 1 ppm $Na_2S_2O_3$
   b) Borated water + 200 ppm N_2H_4 and thiosulfate

3. Sulfate Contamination
   a) Borated water + 100, 10, 1 ppm Na_2SO_4
   b) Borated water + 100 ppm N_2H_4 and sulfate

f. Test Temperatures

Test temperatures of 100°F, 130°F, 170°F and 550°F are being used.

2. Arrest the Attack

a. Purpose

Once the aggressive environments are determined, tests will be conducted to determine if various proposed changes will prevent the attack from proceeding.

b. Test Material

The test material is Alloy 600 OTSG tubing with a heat treatment equivalent to TMI-1 (i.e., mill annealed plus 1150°F/18 hours). Some tests will also be done with solution annealed plus stress relieved and actual TMI-1 tubing.

c. Test Specimens

Stressed tubular tensile specimens.

d. Test Method

The causative environment will be used to partially crack the Alloy 600 test specimens - which are loaded in tension - a load cell is used to reflect cracking. Several possible fixes will then be tried to determine if cracking can be stopped from continuing; this would be indicated by no further drop off in load.

e. Possible Fixes

1) Dry layup with dry air

2) Add chemicals to boric acid solution that may react with the sulfur

3) Add $LiOH_2$ to boric acid

4) Gaseous ammonia in dry air

5) Sodium tetraborate (soak)

6) Heat-up to 250°F to oxidize $S - SO_4$ in presence of primary water

7) Heat-up to 250°F to oxidize $S - SO_4$ in presence of dry air

3. Verify the Cracking Scenario

   a. Purpose

   As set down in Section X of this report, a scenario defining the
   probable cause of failure has been established. In order to
   verify this scenario, testing is being performed to duplicate
   those circumstances.

   b. Test Material

   The material is actual TMI tubing and Inconel 600 archive tubing
   with a heat treatment equivalent to TMI-1 (i.e., mill annealed
   plus 1150°F/18 hours).

   c. Test Methods

   Utilizing C-rings, bent longitudinal tube strips and full section
   tubing, the actual hot functional thermal cycle is being dupli-
   cated with the exact primary system water chemistry at that
   time. To this chemistry is added 1 ppm sodium thiosulfate
   contamination up to a maximum of 10 ppm. In addition, tests will
   be conducted with sodium sulfate contamination in the 1-10 ppm
   range.

4. Determine That Cracking Will Not Restart

   a. Purpose

   The purpose is to establish if the sulfur film on tubing surfaces
   or in intergranular attacked areas can produce additional damage
   under aqueous shutdown or operating conditions.

   b. Test Material

   Actual TMI tubing samples with and without sulfur removal.

   c. Test Method

   Tests will be conducted using C-ring and bent beam speci-
   mens placed in primary coolant with Boron concentrations repre-
   sentative of variations which occur during core life. Diluted
   sulfate and chloride contaminants will also be introduced into
   some test environments. These tests will be conducted at 170°F
   and 550°F.

5. Assess Effects of Tube Repair Techniques on Material Resistance to IGA

   a. Purpose

   Repair techniques which involve expansion and/or rolling of the tubing within the tubesheet will introduce additional residual stresses into the tube. Tests will be conducted to assess if the final repair configurations will affect tube performance from corrosion standpoint.

   b. Test Material

   The test material is actual TMI tubing material with and without intergranular cracks and with and without I.D. surface cleaning.

   c. Test Method

   Tests will be conducted on specimens which mock up the repair configuration and subject the sample to typical operational temperatures and environments. Additional environments will include secondary side chemistry with caustic and primary side chemistry with diluted sulfate and chloride contamination.

B. Conclusions

   1. To date, early cracking tests have shown that the cracking mechanism is not currently active in the cleaned up primary coolant.

   2. The presence of an inert atmosphere reduces cracking tendency.

   3. Sulfate at low temperature will not cause cracking under oxidizing conditions.

   4. Thiosulfate at low temperature will cause cracking under oxidizing conditions.

   5. Archive Material in the mill-annealed and stress relieved condition has cracked in 5 ppm thiosulfate, but not in 1 ppm thiosulfate, indicating a threshold concentration requirement greater than 1 ppm.

X   PROBABLE CAUSE OF FAILURES

A.   Introduction

In this section of the report an attempt will be made to combine
the results reported in the other sections into a coherent failure
scenario which can explain the major features of the OTSG tube cracking
phenomenon and is consistent with what is currently known about the
OTSG fabrication and operating histories. Additionally, the implica-
tions of the failure scenario with regard to plant recovery activities
are noted and recommendations based on the conclusions in this report
are presented.

B. Development of a Cracking Scenario

The occurrence of intergranular stress assisted cracking (IGSAC)
requires that three conditions be satisfied simultaneously:

o   a sufficiently high tensile stress
o   a susceptible material microstructure
o   an aggresive environment.

The information presented in the other report sections relating to
these three factors is summarized below.

1.   Tensile Stress

Section VIII presents information about OTSG tubing
stresses. Since the cracks are oriented circumferentially in the
tubes, axial tensile stresses are of principal interest. Both
operating and residual stresses must be considered since both can
play a role in IGSAC (for example, both categories of stress are
involved in IGSAC of BWR stainless steel piping). Cracking must
have occured in a situation in which the sum of the operating and
residual stresses in the axial direction was greater than that in
the hoop direction otherwise the crack orientation would have been
axial. The Section VIII analyses indicate that this condition is
satisfied during cooldown and cold shutdown. Highlights of the
stress analysis from the failure scenario viewpoint are:

a. Tubing axial tensile stresses are largest during cooldown
   when they may approach the yield stress.

b. Significant axial tensile stresses also exist during cold
   shutdown.

c. Locally high axial tensile stresses are possible in the seal weld heat affected zone and in the vicinity of the roll transition.

d. Under heatup and at full operating temperature the hoop stress generally is larger than the axial stress.

e. The axial stresses are generally larger at the periphery than in the center of the tube bundle.

Thus, the stress analysis results suggest that the cracking must have occurred during cooldown or during cold shutdown. The stress analysis also explains why the seal weld heat affected zone and the roll transition region should be particularly prone to cracking and why more cracking occured in the periphery than in the center of the tube bundle.

2.   Susceptible Material Microstructure

The OTSG fabrication history is documented in Section VII. The fabrication history puts the tubing into service in the mill annealed plus stress relieved condition which is expected to be heavily sensitized (i.e., low grain boundary chromium content). Metallurgical examination has confirmed that the expected micro- structure is present. Thus, the fabrication history results indicate that the tubing microstructure was highly sensitized, and therefore susceptible to attack by water containing sulfur oxyanions.

3.   Aggressive Environment

The results presented in Section V indicate that sulfur was present in the primary system water and three possible sources of sulfur have been identified from the OTSG chemistry history (Section IV). As indicated in the discussion presented in Section IV, if SO_4^{--} and S_2O_3 were introduced to the primary water as the OTSG operating and chemistry histories suggest, they would be expected to persist as long as the water was at room tempera- ture even if the oxygen content of the water was reduced by hydra- zine additions. However, hydrogenating and heating the water to perform a hot functional would be expected to result in the generation of S^{--}, possibly accompanied by S and other inter- mediate species. Subsequent cooling to room temperature and oxygenating following the hot functional would rapidly oxidize S^{--} to S and could also result in the appearance of significant concentrations of other species of higher oxidation states. Although it is not possible to predict either the identities or

the concentrations of the sulfur species present following the hot functional, it is clear that this transient is likely to have greatly affected the aggressiveness of the environment with regard to low temperature sulfur-induced attack of the OTSG tubing.

4. Proposed Failure Scenario

The discussions presented above suggests that the probable cause of failure was as follows:

a. During layup the primary system was contaminated with sulfur by the accidental introduction of sulfuric acid, sodium thio-sulfate, and possibly a sulfur-containing oil. The amount of sulfur present may have reached several ppm, but the con-taminated water was not aggressive enough to crack mill annealed plus stress relieved Alloy 600. The cracking tests confirm that cracking would not have been expected to occur at this stage.

b. The temperature and oxidation potential transient associated with the hot functional test resulted in a change in the types and concentrations of sulfur species present in the primary water. Further changes occured when thiosulfate-contaminated water was injected during the tests of the HPI and LPI systems.

c. When the water level in _he OTSGs was lowered following the hot functional, high concentrations of aggressive metastable sulfur species developed in the dry-out region at the top of the generators due to the combined effects of solution con-centration by evaporation and the comparatively high avail-ability of oxygen. Changes in the sulfur species in the more dilute bulk solution proceeded more slowly resulting in lower concentrations of aggressive sulfur species.

d. Sulfur-induced IGSAC of the Alloy 600 tubing occurred rapidly in the dry-out zone with preferential attack at high stress locations. Little or no cracking occurred below the water line because the bulk solution was less aggressive.

e. Cracking terminated either because continued chemistry changes resulted in the formation of less aggressive sulfur species or because the environment in the dry-out region was diluted by the slowly-rising bulk solution. By the time the water level was dropped again, the chemical state of the sulfur in the primary water was sufficiently different from its state immediately after the hot functional to prevent a full scale recurrence of steps c and d in the new dry-out zone.

f.   Cracking was discovered when the OTSGs were pressurized.

5.   Eddy-Current Indications Below the Surface

The recent eddy-current indications of defects below the initial water surface requires special mention.

The fact that eddy-current indication at about the 1 volt level was observable at the 3rd Tube Support Plate (TSP) +3" in tube A 149-34 on 5/7/82, but not at that location on 4/17/82, implies that either cracking is still taking place or that earlier eddy-current examination did not detect this particular defect. The flaw growth program indicates that detection repeatibility of 1 volt and less signals is about 75% (Reference 12).

The possibility therefore exists that the indicated defect existed but went undetected on the 4/17/82 examination. The fact that all known I.D. defects as called by eddy-current testing are greater than 50% through wall with the majority nearly through wall and that the flaw growth program revealed no new defects with signals greater than 1 volt, indicate that cracking is not an on-going process.

As indicated in the above failure scenario, the sulfur promoted intergranular stress assisted cracking responsible for the observed defects in the OTSG tube depends on a concentration of aggressive sulfur species, which appears to exist only temporarily during a reduction-oxidation cycle of the solution present in the reactor coolant system during hot functional testing. It is unlikely that this concentration of aggressive sulfur species would persist some months after the tubes were exposed to atmospheric oxygen and then suddenly initiate cracking. The OTSG tubes below the 7th TSP were re-wet on 4/6/82 with water which was analyzed on 4/26/82 to have 24 ppb sulfate and 1.06 ppm lithium. That solution remained at that level until 5/9/82, when the OTSG was again drained. In the absence of another reduction-oxidation cycle and in the presence of the benign solution described above, it is probably that the defect was not initiated subsequent to 4/17/82.

The question remains as to how a crack might have been initiated below the initial dryout zone. The region of the OTSG tubes above the water level immediately following hot functional testing (about 9/8/81) was down to about the 13th tube support plate. The vast majority of defects are in this region. Water level slowly increased until it was above the upper tube sheet on 9/27/81.

It is supposed, as indicated in the failure scenario, that rapid oxidation of the solution left on the exposed tubes led to significant concentrations of aggressive sulfur species and hence the widespread attack on the tubes. Oxidation of the bulk solution would have proceeded much more slowly, yielding a less aggressive environment. In fact, it now appears that oxidation of the bulk solution may have been even slower than at first thought, such that some reduced sulfur species persisted until water level reductions on 10/6/81 and finally draining of the OTSG in early December 1981 exposed a thin film of the bulk solution to an oxidizing environment. The resulting concentration of metastable sulfur species, while much less damaging than the initial solution, could cause isolated attack on the OTSG tubes.

Alternatively, the bulk solution may have oxidized more rapidly than originally thought, again resulting in a marginally aggressive solution below the water surface, decreasing in aggressiveness with depth such that the high stress regions associated with the lower tube sheet were protected.

The proposed failure scenario does not require that there be no defects below the initial water surface. In fact, the total absence of such defects would require a rather special oxidation rate of the bulk solution, as suggested by the foregoing discussion. The existence of the special oxidation rate is plausible but its absence is not surprising.

6. Scenario Summary

This scenario is consistent with all of the observed features of the cracking phenomenon (with the possible exception of the non-axisymmetric radial distribution of cracking in OTSG-B) and is also consistent with the timing of the cracking and the results of the metallurgical examinations and corrosion tests. Clearly the key feature of the scenario is the generation of a highly aggressive, transient environment following the hot functional test.

7. Implications with Respect to Plant Recovery

The scenario proposed above suggests that the cracking process could be reactivated by the temperature and oxidation potential transients that are likely following repair during preparations for plant start-up unless the inventory of sulfur in the primary system is reduced to a low level and positive steps are taken to prevent recontamination. Accordingly, an attempt should be made to remove sulfur-containing surface films from the OTSG tubing and other primary system surfaces. Oxidation to generate soluble sulfur species followed by removal via demineralization is thought to be the most promising approach.

D. Conclusion

A scenario based on IGSAC by metastable sulfur species in the period immediately following the hot functional test can explain the major features of the OTSG cracking phenomenon and is consistent with the findings of the various activities undertaken by the Failure Analysis Task Group.

E. Unresolved Questions Raised by Failure Analysis

1. What caused the distribution of damage in the B OTSG?

   a. The damage is probably stress related.

      1) There is no clear difference in environment.

      2) There is no clear difference in material.

      3) There is clear stress dependence in A OSTG.

   b. The detailed answer to the questions will not impact:

      1) Plant recovery.

      2) Subsequent operations.

   c. Further study of this question will be carried out following the closeout of the Failure Analysis Task, and the Final Report.

2. What role, if any, did oil play in the OTSG damage?

   a. Oil was not the sole source of the damaging sulfur. In fact, it is unlikely that any sulfur was released from the oil available for introdution into the Reactor Coolant System (RCS).

   b. One cannot say with certainty what effect if any that oil, if present in the (RCS), had on the OTSG.

   c. The detailed answer to the question will not impact:

      1) Plant recovery.

      2) Subsequent operations.

   d. Further study of this question will be carried out following the closeout of the Failure Analysis Task, and the Final Report.

F. Recommendations

1. Additional water samples should be taken and analyzed for sulfur levels below .1 ppm, to better quantify existing sulfur levels.

2. A cleaning program should be conducted to remove sulfur contamination in the RCS and related systems. Cleanup is necessary to prevent subsequent damage to equipment resulting from sulfur attack. A sampling program is recommended to verify the effectiveness of the cleaning process relative to sample results from 1. above.

3. Repair procedures and programs should be based on the consideration that currently known eddy-current defects are 100% through wall or will be through wall after several thermal cycles due to fatigue of the remaining ligament.

4. Based on the sulfur species present, in addition to the system cleanup of step 2. above it may be necessary to take steps to remove the surface films if they are in a form which could reactivate and become corrosive. Additional cracking tests scheduled will aid in making this decision.

5. Materials utilized in the repairs of the steam generators, need to be carefully specified to assure a material which would have adequate immunity to future corrosion problems. In addition, these materials need to be qualified by acceptable techniques to assess the degree of sensitization.

6. Plant operational chemistry specifications should be revised to address control of sulfur in the primary and secondary coolant systems.

7. Steps must be taken to preclude the introduction of chemical contaminants into the RCS and its support systems.

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