PWR STEAM GENERATOR CHEMICAL CLEANING
PHASE II FINAL REPORT
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SAMUEL ROTHSTEIN

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CONSOLIDATED EDISON CO. OF NEW YORK
4 IRVING PLACE
NEW YORK, N Y. 10003

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PWR STEAM GENERATOR CHEMICAL CLEANING
PHASE II FINAL REPORT

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Two techniques believed capable of chemically dissolving the corrosion products in the annuli between tubes and support plates were developed in laboratory work in Phase I of this project and were "pilot" tested in Indian Point Unit No. 1 steam generators. In Phase II, one of the techniques was shown to be inadequate on an actual sample taken from an Indian Point Unit No. 2 steam generator. The other technique was modified slightly, and it was demonstrated that the tube/support plate annulus could be chemically cleaned effectively.

Two techniques believed capable of chemically dissolving the corrosion products in the annuli between tubes and support plates were developed in laboratory work in Phase I of this project. These are listed in Tables 2-1 and 2-2. Each was "pilot" tested in a horizontal B & W steam generator in Indian Point Unit No. 1, along with samples simulating what was believed to be the condition in the vertical Westinghouse steam generators in Indian Point Unit No. 2. Both techniques appeared to be effective.

In order to better identify the conditions in the Unit No. 2 steam generators, and to ensure that the solvents would be effective in the steam generators, a sample, consisting of a portion of a support plate including undisturbed tube stubs and associated corrosion product, was removed from one Unit 2 steam generator, and sludge was removed from all four Unit 2 steam generators.

Laboratory tests were conducted to evaluate the capability of the two solvents to dissolve the sludge. It was found that with the citric/ascorbic solvent (Table 2-1) only up to 60% of the sludge was dissolved. By modifying some of the parameters, the percentage was increased to 85%. This was considered inadequate, and the solvent was rejected. It was found that with the EDTA/citric solvent (Table 2-2) 86% of the sludge was dissolved, and by modifying some of the parameters, this percentage was increased to 94%. This was considered acceptable.

Consequently, the modified EDTA/citric solvent (listed in Table 5-3) is recommended.

Laboratory testing was continued using a tube stub with a "star-shaped" piece of support plate attached (which had been removed from the Unit 2 steam generator). It was found that the quiescent solvent was not effective in dissolving the corrosion products in the tube/support plate annulus, but that a flowing solvent was effective.

Vibration and wear tests were undertaken to establish the effect of anticipated post-cleaning conditions on the serviceability of the steam generators. It was found that for the small radius U-bend tubes, increasing the tube to support plate clearance from 15 mils radial to 40 mils radial resulted in only minor changes in acceleration response levels.

The project was terminated before further testing was completed. The principal reason for termination was that it is not possible to establish the condition of the support plates in the Indian Point Unit No. 2 steam generators to the extent where it would be possible to proceed with chemical cleaning with assurance that the steam generators in the post-cleaning condition would be serviceable. Further details as to the technical reasons why it was not possible to proceed with the actual chemical cleaning are presented in paragraph 4.2.6 and Appendix A of this report.

TABLE 2-1 CITRIC/ASCORBIC SOLVENT

1. Sludge Iron Solvent

Citric Acid	10%
HEEDTA	1%
Diethyl Thiourea	0.3%
Triton X-100*	0.05%
Chevron N1-W**	0.01%
pH	3.5-3.7
Temperature	185°F

2. Sludge Copper Solvent

Add to Sludge Iron Solvent:

Ammonium Hydroxide	as required
Sodium Nitrite	1%
pH	9.5
Temperature	140°F
Air Sparge	

3. Crevice Iron Solvent

Citric Acid	3%
Ascorbic Acid	3%
Diethyl Thiourea	0.3%
Triton X-100	0.05%
Chevron N1-W	0.01%
pH	3.5
Temperature	185°F

4. Final Copper Solvent

Add to Crevice Iron Solvent:

Ammonium Hydroxide	as required
pH	10
Temperature	140°F
Air Sparge	

5. Passivation

Add to Final Copper Solvent:

Hydrazine	0.1%
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* Triton X-100 is iso-octyl phenoxy polyethoxy ethanol with 10 moles ethylene oxide.

** Chevron N1-W is ethoxylated alkyl phenol.

TABLE 2-2 EDTA/CITRIC SOLVENT

1. Sludge Iron Solvent

EDTA	4%
OSI-1*	0.1%
pH	6-7
Temperature	200°F

2. Sludge Copper Solvent

Add to Sludge Iron Solvent:

Ammonium Hydroxide	as required
Sodium Nitrite	0.5%
pH	9.5
Temperature	140°F
Air Sparge	

3. Crevice Iron Solvent

EDTA	8%
Citric Acid	4%
OSI-1	0.6%
pH	4.2
Temperature	200°F

4. Final Copper Solvent and Passivation

Add to Crevice Iron Solvent:

Ammonium Hydroxide	as required
Hydrazine	0.5%
pH	8

*OSI-1 is a Halliburton proprietary inhibitor. It is an alkyl thiourea.

The steam generators in modern commercial nuclear power plants and the corrosion problems associated with them were described in Volume 1 of the Phase 1 Final Report on PWR Steam Generator Chemical Cleaning (HCP/W4325-01/1 and 01/2 by S. Rothstein and P.F. McTigue, dated July 1978.

Briefly, the most significant problem is that corrosion products in the crevices between the Inconel tubes and the carbon steel support plates are causing deformation of the tubes, and deformation and cracking of the support plates. In one instance, Virginia Electric Power Company has replaced the steam generators in their Surry 2 nuclear power plant, and is preparing to replace those in the Surry 1 plant. Other utilities are also preparing to replace the steam generators in their plants.

Early in 1977, Con Edison placed a high priority on the development of a technique for chemically cleaning the secondary side of the PWR steam generators in order to avoid the need to replace the steam generators at the Indian Point nuclear power plant, and in September 1977, Con Edison entered into a development contract with ERDA (now the Department of Energy) to develop a technique for chemically removing the corrosion products in the annuli between the steam generator tubes and the support plates.

The development program was planned in two phases, as follows:

PHASE 1

1. Evaluate cleaning solvents and procedures.
2. Develop procedures for cleaning Indian Point Unit No. 1 and No. 2 steam generators.
3. Design and install facility modifications needed to accomplish chemical cleaning.
4. Chemically clean Indian Point Unit No. 1 steam generators No. 11 and 12.
5. Evaluate cleaning procedures with reference to applicability to Unit No. 2 steam generators.

PHASE II

1. Refine procedure for chemical cleaning Indian Point Unit No. 2 steam generators, and test in cleaning model(s) employing actual sludge and actual tube/support plate intersections.
2. Design and install facility modifications needed to accomplish chemical cleaning.
3. Chemically clean Indian Point Unit No. 2 steam generators.

All tasks under Phase 1 were completed and were reported in the Phase 1 Final Report dated July 1978.

The Phase 1 evaluation of the cleaning procedures developed resulted in a recommendation that before proceeding with Phase II the following additional areas be evaluated:

1. Corrosion rates of the materials of construction of the steam generator in the solvents selected with representative amounts of sludge taken from an operating steam generator.
2. Efficiency of solvents on actual tube/support plate crevice corrosion products, as evidenced by test on samples taken from a steam generator.
3. Effect of solvent on welds and heat affected zones of welds of the materials of construction in the steam generator.
4. Effect of solvent velocity on dissolution of corrosion products and on corrosion of base metals.
5. Effect of solvent residuals on steam generator materials during post-cleaning operation.
6. Capacity of solvent for dissolution of sludge based on tests on sludge removed from a steam generator.
7. Improved techniques for handling large volumes of low activity waste solvent and rinse waters.

Items 1, 2, 4 (in part) and 6 were undertaken and are reported herein. Because of the early termination of this project, item 3, 4 (balance), 5 and 7 were not accomplished.

Task 1 of Phase II was carried out in steps as follows:

- Actual removal of sludge and tube/support plate samples from the Unit 2 steam generator. (Discussed in Section 4.0)
- Dissolution tests on sludge. (Discussed in Section 5.0)

- Laboratory chemical cleaning of tube/support plate sample.
(Discussed in Section 6.0)
- Evaluation of results. (Discussed in Section 9.0)

To supplement the staff assigned to this program, Con Edison retained NUS Clearwater to develop electro-discharge machining (EDM) tooling specifically for cutting the tubes and the support plate.

In addition to the work described above, it was determined that an additional evaluation should be made of the effect on tube vibration and wear of increased clearances between the tubes and the support plates as would probably result from a chemical cleaning of the steam generators. To supplement the facilities available at Con Edison, Wyle Laboratories was retained to conduct flow and vibration studies. (This work is discussed in Section 7.0)

Tasks 2 and 3 of Phase II were not completed because of the decision not to proceed with the chemical cleaning of the Unit No. 2 steam generators, as explained on page 2-2.

Introduction

Sludge removal from nuclear steam generators by hydraulic lancing has become routine. However, removal of a tube/support plate sample from the body of the tube bundle in a nuclear steam generator had not been accomplished before, and a new technique and new tooling had to be devised. This section describes the development of procedures and equipment utilized for removal of the sample, as well as the evaluation of the sample.

4.1 Sludge Removal and Sampling

Sludge was removed from each of the steam generators using "standard" Westinghouse Electric Corp. equipment and procedures. The procedure consists of using a high pressure demineralized water jet to break up and slurry the sludge, and removing the slurry from the steam generator via a peripheral suction line. The slurry is passed through filtration equipment. The filtrate was discarded, and the sludge was retained for further testing.

4.2 Tube/Support Plate Sample Removal4.2.1 Removal Plan

Samples of tubes and support plates had previously been removed at other utilities by Westinghouse Electric Corp. These samples were wedge shaped segments from the

periphery of the top support plate. Entry into the shell via the upper manway and steam separator deck was necessary in order to remove the sample.

For the chemical cleaning tests, a tube/support plate sample from the body of the bundle was desired. Therefore it was decided to take a sample from the tube lane region of the lowest support plate.

It was proposed that two new 8" diameter handholes would be provided - one at the level of the lowest support plate, and the other below the level of the next upper support plate. These (plus the existing 6 inch handhole above the tubesheet) would provide access to cut and remove tubes above and below the lowest support plate, and to cut out the desired sample. The handholes would then be closed with a blind flange. Figure 4-1 is a sketch of the proposed configuration, and Figure 4-2 is a photo of the proposed sample.

Although provision of the new 8 inch handhole openings would require weld build-up for reinforcement around the opening, the welding and machining were straightforward, and required only some practice in working in the restricted areas adjacent to the steam generator. Cutting the tubes and the support plate required development of a technique and special tooling.

Figure 4-1
Location of New Handholes in Steam Generator

Figure 4-2

Proposed Sample, as Cut from Mock-up

4.2.2 Evaluation of Cutting Techniques

Mockups of the steam generator lowest support plate were reviewed and some preliminary discussions were held on the following approaches:

- a) Electrical Discharge Machine (EDM) cutting of the tubes and support plate.
- b) Mechanical cutting of the tubes, (slitting saw, shear, etc).
- c) Mechanical cutting of the support plate ligaments by broaching or sawing.
- d) Oxy-Acetylene cutting of the support plate.
- e) Plasma torch cutting of the tubes.

A detailed description of each concept is given below:

4.2.2.1 EDM Cutting of the Support Plate and Tubes.

Although normal in-shop EDM machining is performed with the work submerged in and flushed with oil, on occasion EDM cutting is accomplished using only a water flush. Cutting times are not as fast, finishes are poorer and electrode wear could be expected to be higher than for shop conditions.

Demonstration cuts were made on tube samples using only an oil flush and a vertical electrode. Cuts were made in about four minutes and produced an excellent finish with no burrs. Comparable tests using a water flush system indicated the following:

- a) Cutting times were substantially increased over what would be expected for normal production type cuts.
- b) Normal tap water was unacceptable.
- c) Electrode wear was very high.
- d) The cutting speed and electrode wear were very sensitive to machine parameters.
- e) Tube cuts and support plate ligament cuts could be made.
- f) The cut edges were burr-free.

Tests were also performed to evaluate using an air blast or a water and air mist for flushing. Both proved unsatisfactory as it was not possible to make a cut.

4.2.2.2 Mechanical Tube Cutting

Pneumatic slitting saws and cutoff wheels, and mechanical tube cutters were investigated. However, none of the mechanical approaches was pursued for one or more of the following reasons:

- a) The steam generator space was too confining for proper equipment operation.
- b) Mechanical vibration or force on the tubes would alter the corrosion product at the tube-to-plate interface.
- c) The probability of causing damage to adjacent tubes was high.

- d) Cutting concepts produced cuts that required deburring or other operations in order to plug the tube ends.

4.2.2.3 Mechanical Support Plate Cutting

Mechanical cutting of the support plate could be performed by cutting the flow hole-to-tube hole ligament in a zig-zag manner along a row adjacent to the desired sample. Various broaching and cutting techniques were considered but none were considered feasible due to one or more of the following reasons:

- a) The steam generator space was too confining for proper operation of the equipment.
- b) Possible damage could occur to adjacent tubes and tube sheet areas.
- c) Mechanical force and vibration could affect the corrosion product on the tubes and plate.
- d) This required cutting an additional row of tubes beyond those which were in the sample section.

4.2.2.4 Oxy-Acetylene Cutting of the Tube-to-flow Hole Ligaments in the Support Plate

Because of the restricted area, the use of off-the-shelf torches was not feasible. A cutting head was modified to properly position the tip for the ligament cut.

A sample support plate with tube stubs was made up for test purposes. Using the modified torch head, it was possible to cut the ligaments without harming the adjacent to tube stubs.

4.2.2.5 Plasma Tube Cutting

The standard plasma arc torch would not satisfactorily make repeated cuts through both walls of the tube. Modifications were required and the cut was extremely rough and would require considerable cleanup before a plug could be installed. This concept was not pursued further.

4.2.2.6 Conclusion

Review of the concepts considered led to the decision to proceed with the EDM approach. The principal reasons why this technique appeared the most attractive were as follows:

1. The EDM technique is precise and easily controlled. The danger of damaging other steam generator components is minimized.
2. The tube cuts are clean and require the minimum amount of cleanup.
3. EDM uses a thin electrode with minimum overcut. As such, it is capable of cutting between the second and third tube rows without damaging either row. This will permit removing a two-row sample without having to take the third tube row out of service.
4. The EDM electrode does not contact the part being cut. Therefore, it has minimal effect on the plate and tube corrosion product.

4.2.3 Prototype Development

4.2.3.1 Equipment Procurement

Equipment available from different EDM manufacturers was evaluated. This evaluation included:

- a) Delivery time compatible with the tight schedule.
- b) Equipment physical size and weight required for movement.
- c) Ability of vendor to provide adequate and speedy field support.
- d) The price.
- e) The flexibility of the design and the ease with which it could be adapted to the specific needs.
- f) The features offered which would provide more flexibility in achieving maximum cutting speed.

Based on this evaluation, equipment manufactured by Hansvedt Engineering was selected. The Hansvedt equipment is intended for in-shop use, but very little modification was required to achieve a design which met the needs. This system consisted of:

- a) A 20 amp power supply and machine control unit.
- b) A 20 amp booster power supply to increase the total available power to 40 amps.
- c) A hydraulic power system. (The seals in the hydraulic equipment were changed so a high temperature fire resistant hydraulic fluid could be substituted for the petroleum base fluid normally used.)

- d) A hydraulic ram and servo system. The servo system was replumbed to produce a more compact unit which would mount directly on the EDM cutting head.
- e) The hydraulic lines, electrical control leads, and electrode power leads were increased to 50 ft. in length to permit remotely locating the power units away from the steam generator (in potentially lower radiation level areas).

4.2.3.2 Mockup Modifications

The mockup included a shell containing the lower 6 inch handhole, the 8 inch handholes (which were to be added to the generator by Con Edison), and a simulation of the support plate, which included the first flow slot and adjacent tubes. The support plate was modified to include a replaceable section to permit repeated development cuts.

4.2.3.3 Prototype Equipment Development and Tests

Design layouts were made for an EDM electrode positioning device which bolted to the steam generator flange at the 8 inch handhole. The equipment could be oriented either horizontally or vertically, for tube or support plate cutting. The device utilized a small machine slide to which the EDM hydraulic servo system was attached and a mounting block, which positioned the electrode holder,

consisting of a 1 inch diameter tube closed at both ends. Short lengths of 1/4 inch diameter tubing bent to various shapes to correctly locate the electrode could be attached to the end of this holder. A special electrode clamp was attached to the outer end of this tube. The clamp held the electrode and, through special slots, allowed the flow of flushing water over the electrode surfaces. A flow of demineralized water was supplied through the center of the electrode holder. A demineralized water (resin bed) system was secured to supply a source of flushing water for the tests.

Using the equipment described above, a series of tests were performed to evaluate various electrode materials and machine settings. The following materials were evaluated for both the tube and support plate cuts:

- a) Various grades and densities of graphite.
- b) Copper-impregnated graphite material.
- c) Copper-tungsten alloy.
- d) Tungsten.
- e) Copper sheet.
- f) Brass.

These materials were evaluated by using various combinations of electrode polarity, spark frequency, power on-time, electrode speed, and system capacitance.

The electrode wear was high relative to what is normally achieved in a machine shop setup. In order to achieve reasonably fast cutting speeds, the machine was run at a setting of 200 amperes per sq. in. of electrode instead of the machine-shop-recognized limit of 50 amps per sq. in. This use caused high electrode wear, making it desirable to change the electrode after each cut in order to minimize alignment and electrode starting problems. High electrode wear could then be accepted.

The following parameters and materials were selected as a result of this testing. (The setting numbers refer to the Hansvedt Control Positions):

	<u>Plate-Cuts</u>	<u>Tube Cuts</u>
Electrode Material	Copper-Tungsten	Graphite
Electrode Polarity	Normal	Normal
Ram Speed Setting	7	7
Power on Time Setting	70%	70%
Frequency Setting	8	2
Capacitor Addition Setting	12 MF	None
Flush Flow Rate	1 gpm	1 gpm
Time Required Per Cut	13-18 minutes	6-8 minutes

Although it was intended to plug all cut tubes at the tube sheet face using Westinghouse explosive plugs, it was desired to plug the open tube ends inside the steam generator as a further precaution against primary-to-secondary leaking. The following concepts were considered as a means of achieving this:

- a) Mechanically deforming the tube ends to prevent passage of the explosive plug.
- b) Brazed in-place plugs.
- c) An expandable mechanical plug.

A mechanical plug design which could be inserted into a cut tube end and then expanded by torquing was developed. Torquing the top nut of the plug caused expansion of an inner ferrule and deformed the steam generator tube into retaining grooves cut into the tube plug outer sleeve. A test plug was fabricated from stainless steel and installed on a steam generator tube sample. The plug-tube assembly was internally hydro-tested to 5000 psi with no leakage. It was thermally cycled to 600 F and retested successfully. The test piece was then sectioned to observe the deformation of the tube wall.

4.2.4 Equipment Design and Fabrication

Using the information gained from the prototype test, the design and fabrication of the reference design equipment to be used at Indian Point Unit No. 2 was initiated. Work in this phase consisted of designing, fabricating and testing all the equipment necessary to cut the sample from the support plate, and remove it from the steam generator. A detailed description of the equipment is given below.

4.2.4.1 EDM Machine Description

The reference design EDM machine was similar to the setup which had performed successfully in the prototype test. The bracket which bolted to the flange was replaced with one fabricated from heavier angle iron. Square stainless tubing was substituted for the electrode holder. A new electrode holder clamp was fabricated and attached to the machine slide. This clamp incorporated features permitting quick change of the electrode holder and a detent pin type locating device to insure accurate positioning of the electrode. A linear variable displacement transformer (LVDT) digital readout was added to provide remote indication of the slide position and the cutting progress. The 1/16 inch thick copper tungsten electrodes were modified to make positioning in the electrode holder foolproof. The back portion of the electrode was relieved to provide clearance and improve flushing. Three electrode holders were fabricated, one for each of the different type cuts (wide and narrow end cuts and side ligament cuts). Each holder had the properly-located detent holes and electrode clamp to preposition it for its intended type of cuts.

4.2.4.2 Demineralized Water System

A portable demineralized water system was designed and fabricated to support the EDM machine. The system consisted of two commercial resin bed cannisters, a flow

meter, filter, and the necessary valves and plumbing. The entire system was assembled into a box which was also used for shipping.

4.2.4.3 Plate Clamps

Two screw-actuated clamps were designed and fabricated to clamp the support plate sample and hold it firmly in place while the last ligament cuts were made. The clamps were attached to handles so they could be installed remotely from outside the handhole.

4.2.4.4 Sample Lowering Tool

A tool was made to lower the sample, once it was cut, from the support plate to the lower 6 inch handhole so that it could be removed from the steam generator. (Due to space restrictions, the sample could not be removed through the 8 inch handhole). The lowering tool consisted of a manually-operated winch and cable device which bolted to the top 8 inch handhole. An arm and pulley extended into the steam generator to position the cable over the center of the sample. A threaded weight was attached to the end of the cable. In use, the cable was lowered from the top handhole until it was visible just above the support plate sample. It was grasped and pulled from the steam generator and the threaded weight removed. The end was then placed through a flow hole in the sample, brought outside the generator, and the weight reattached. The cable slack was taken up sufficiently to support the plate.

4.2.4.5 Sample Removal Tool

A tool was designed to reach through the 6 inch handhole, grasp the sample and remove it from the generator. The tool consisted of two concentric tubes with knurled posts attached to the inner ends. The tool was approximately 5 ft. long and had a means of locking the concentric tubes located on the outer end. In use, the tool was inserted through the 6 inch handhole and the knurled posts were inserted through two adjacent flow holes in the sample. The posts were forced against the flow hole edges and locked in place by the external handle, securely grasping the sample so it could be removed through the 6 inch opening.

4.2.5 Removal of Sample

Crews were trained in the procedures necessary to remove the sample on a mock-up in the shop.

Weld reinforcements were deposited as necessary, and the 8 inch handhole openings were machined. EDM tooling was positioned and tubes and support plate were cut as planned. The sample was lowered to the level of the 6 inch handhole, but as it was being removed from the steam generator, it separated into a number of pieces, as several of the ligaments had been cracked. Figure 4-3 is a photograph of the sample as removed.

Figure 4-3

Support plate sample and pieces as removed from Steam Generator 23, Indian Point 2.

A report of the detailed analysis and study of a tube stub and a support plate segment by Payer, White and Berry of Battelle Columbus Laboratories is contained in Appendix A.

4.2.6 Evaluation of Sample

Prior eddy current examination of the steam generator tubes contained in the sample had indicated minor denting of the order of 0.003" to 0.005". Mechanical measurement of the tubes after the sample was removed revealed that they were as much as 0.050" out of round. Further, the edge of the sample which had been fabricated as a reasonably straight edge was found to bowed approximately 0.3".

As explained in the Phase I report, it was postulated that the corrosion products in the annuli, being more voluminous than the steel from which it was formed, produce compressive stresses on the surfaces of the drilled support plate holes. Cumulatively, these expansive stresses result in an in-plane growth of the support plate. Where these stresses are not balanced, as along the edge of the flow slot, they result in a bowing of the flow slot edge with extension and cracking of the ligaments in the region of greatest bow.

It was observed that other flow slot edges in the steam generators were similarly bowed. In the absence of a non-destructive examination technique to demonstrate

conclusively that other ligaments were or were not cracked, there was a concern that if the steam generators were chemically cleaned, segments of cracked ligaments could be loosened from the parent support plates and, as loose pieces, might damage adjacent tubes by vibrating against them. Consequently, it was decided not to proceed with the chemical cleaning of the steam generators and the project was terminated.

Introduction

The Phase 1 development of the solvent utilized simulated sludge produced in the laboratory by mixing appropriate chemicals to match the analysis of sludges removed from other nuclear steam generators. In preparation for cleaning the Unit 2 steam generator, evaluation of the dissolution efficiency of the solvent on actual Unit 2 steam generator sludge was performed. This section describes the dissolution tests for the Unit 2 sludge, and the subsequent modification of the solvent to improve its efficiency.

5.1

Sludge Analyses

The sludge removed from each of the four Unit 2 steam generators was analyzed. Results of the analyses indicated that the material removed from the steam generators was essentially similar to the "laboratory - produced" sludge used in the Phase I testing. Detailed analytical results are listed in Table 5-1.

5.2

Test Procedure

Samples of sludge, each 2.0 grams, were exposed to 1 liter of solvent, following the procedures developed for chemically cleaning the steam generators, in an attempt to dissolve the sludge. At the conclusion of the procedure, the sludge remaining was collected, weighed and analyzed. It was found that the ascorbic acid/citric

TABLE 5-1 SLUDGE ANALYSES

The range of analyses of sludges taken from the different Unit 2 steam generators is:

Fe (as Fe_3O_4)	38 - 69%
Cu (as Cu)	23 - 50%
Zn (as Zn)	1.6 - 2.3%
Al (as Al)	0.2%
Ni (as Ni)	0.7 - 1.2%
B (as BO_3)	1.9 - 2.0%
Chlorides	0.02 - 0.04%
Sulfates	not detected
Phosphates (water sol.)	0.001 - 0.008%
Phosphates (water insol.)	1.8 - 2.7%

acid solvent was less than 60% efficient in dissolving the sludge, and the EDTA/citric acid solvent was over 90% efficient in dissolving the sludge. Minor changes in parameters were made in subsequent tests in attempts to improve dissolution efficiencies. The maximum dissolution attainable with the ascorbic/citric solvent was 85%, while that with the EDTA/citric solvent was 94%.

Table 5.2 lists the solvent parameters changed in each test, and the results of each test.

Table 5.3 lists the composition of the solvent decided upon for further testing on a tube/support plate sample and Table 5.4 lists the procedural sequence.

Table 5-2 Sludge Dissolution Tests

A. Citric/Ascorbic Solvent
(Sludge Iron and Sludge Copper Steps)

<u>Solvent & Conditions</u>			<u>Sludge Copper Stage</u>		<u>Sludge Dissolved</u>
<u>Composition</u>	<u>Sludge Iron Stage</u>				
	<u>Temp °F</u>	<u>p^H</u>	<u>Temp °F</u>	<u>p^H</u>	
Standard-1*	180	3.6-3.7	140	10.1-10.2	46-57%
Standard-1	160	3.7	140	10.4	61%
Standard-1	200	3.7	160	10.0	66%
Standard-1	180	3.7	160	9.9-10.1	61-76%
Standard-1	180	3.7	140	9.7	49-52%
No HEEDTA	200	3.3	160	10.0	80%
No HEEDTA	180	3.6	140	9.7-9.9	71-85%
No HEEDTA	180	5.7	140	10.2	41-43%
No HEEDTA	180	7.2	140	10.1	36-47%

* "Standard-1" refers to solvent compositions given in Table 2-1

B. EDTA/Citric Solvent
(Sludge Iron and Sludge Copper Steps)

<u>Solvent & Conditions</u>			<u>Sludge Copper Stage</u>		<u>Sludge Dissolved</u>
<u>Composition</u>	<u>Sludge Iron Stage</u>				
	<u>Temp °F</u>	<u>p^H</u>	<u>Temp °F</u>	<u>p^H</u>	
Standard-2**	180	5.7	140	10.1	86%
Standard-2	160	5.7-5.9	140	10.1-10.2	51%
Standard-2	180	5.9	145	9.9	61%
Standard-2	200	4.6	160	10.3	93-94%
Standard-2	200	4.8-5.0	160	9.7-10.1	79-92%
Standard-2	200	6.2-6.3	160	9.9-10.0	76-83%
Standard-2	200	7.1-7.2	160	9.9	63-76%
Standard-2	200	9.4	160	10.5	40-45%
Standard-2	200	6.9-7.3	160	9.9-10.5	50-65%
Standard-2	200	7.0-7.1	160	9.3-9.6	67-68%
No Nitrite	200	7.1	140	10.4-10.8	67-74%
No Nitrite	200	7.2-7.3	160	10.2-10.3	63-78%
Only 3% EDTA	200	7.1	160	10.1	58-76%
Only 3% EDTA	200	7.6	160	9.9-10.0	60-69%
Only 2% EDTA	200	6.9	160	9.9-10.0	46-49%

** "Standard-2" refers to solvent compositions given in Table 2-2

TABLE 5-3 MODIFIED EDTA/CITRIC SOLVENT

1. Sludge Iron Solvent

EDTA	4%
OSI-1*	0.1%
pH	4.6-5.0
Temperature	200 F

2. Sludge Copper Solvent

Add to Sludge Iron Solvent:

Ammonium Hydroxide	as required
Sodium Nitrite	1%
pH	10.1-10.3
Temperature	160 F
Air Sparge	

3. Crevice Iron Solvent

EDTA	8%
Citric Acid	4%
OSI-1	0.6%
pH	4.2
Temperature	200 F

4. Final Copper Solvent and Passivation

Add to Crevice Iron Solvent:

Ammonium Hydroxide	as required
Hydrazine	0.5%
pH	8

* OSI-1 is a Halliburton proprietary inhibitor. It is an alkyl thiourea.

TABLE 5-4 CHEMICAL CLEANING SEQUENCE

1. Sludge Iron Solvent
2. Sludge Copper Solvent
3. Drain and Rinse
4. Crevice Iron Solvent
5. Final Copper Solvent and Passivation
6. Drain and Lay-up

Introduction

The Phase 1 development of the solvent utilized simulated tube/support plate samples produced in the laboratory by placing a carbon steel plug and corroded in an Inconel tube and autoclaving the assembly until corrosion products completely filled the annulus between the plug and the tube. This section describes the evaluation of solvent efficiency in cleaning a tube/support plate sample taken from the Unit 2 steam generator. Inasmuch as the efficiency of the Citric/Ascorbic solvent was found to be inadequate, only the EDTA/citric solvent was used in this test.

6.1

Quiescent Solvent Test

It had been demonstrated in the Phase I work that it was necessary to have some flow of solvent across the sample to be cleaned in order to dissolve the corrosion product in the annuli between the tubes and the support plates. However, it was decided to re-evaluate the efficiency of modified solvent in quiescent applications. A tube to which a segment of support plate remained attached was selected as the test piece. This is shown in Figure 6-1. EDTA/citric acid solvent was applied, following the procedure listed in Table 5-3. After 120 hours of cleaning, it was found, as expected, that the quiescent

Figure 6-1

Tube and ligament sections removed from hot leg of steam generator 23.

- a) Tube stub with one of the four surrounding segments missing from "star shape".
- b) "Star shape" with one unfractured ligament between second-row tube hole and second-row flow hole.

solvent was not effective. The tube after "quiescent cleaning" is shown in Figures 6-2 and 6-3. Corrosion coupons accompanying the tube during this test showed nominal corrosion losses.

6.2 Flowing Solvent Test

The same tube/support plate segment used in the quiescent solvent test was used in the flowing solvent test. The flow velocity decided upon was expected to be in excess of the minimum necessary to achieve dissolution of the corrosion product in the annulus. Again, the EDTA/citric acid solvent was applied following the procedures listed in Table 5-3. After 72 hours of cleaning, the tube was separated from the support plate segment. This is shown in Figure 6-4. Although some corrosion product remained on the surface of the tube hole, the test was not continued because it was expected that after the tube was separated from the support plate, and the corrosion product was fully exposed to the solvent, it was only a question of time to achieve complete dissolution of the corrosion product.

Corrosion losses on corrosion coupons accompanying the tube during this test were as follows:

<u>Material</u>	<u>Corrosion Rate</u>
SA 508	6.1, 6.2 mils per day
SA 533	2.5, 6.0 mils per day

The high corrosion rates are attributed to the velocity of the solvent.

Figure 6-2
Tube and Ligament Section as Cleaned in Quiescent Solvent

Figure 6-3
Tube and Ligament Section as Cleaned in Quiescent Solvent

Figure 6-4
Tube and Ligament Section, as Cleaned in Flowing Solvent

Introduction

This section describes the additional work determined to be necessary to evaluate the effect on tube vibration and wear of increased clearances between the tubes and the support plates as would probably result from a chemical cleaning of the steam generators. Due to the early termination of this project only the effect of the projected increased clearances on small radius U-bend tube vibration was evaluated. However the entire scope of the planned program is presented as guidance for possible future work.

7.1 Scope of Testing Program

As a part of Con Edison's steam generator chemical cleaning program, a tube vibration study was planned to investigate the possible changes of dynamic response of the tube and tube support system as a result of chemical cleaning. There is concern that once the corrosion products are removed from the crevices between the tube and tube support plate by chemical cleaning, the annular gap between the tube and its support plate hole may be substantially enlarged and may greatly enhance the vibration potential of the tubes which in turn, may lead to early tube failure.

It is assumed that a properly designed steam generator will not undergo adverse flow-induced vibrations since

good design practice should ensure (1) flow conditions such that minimum fluid dynamic instabilities are encountered, and (2) structural designs with resonances sufficiently removed from the Strouhal frequencies of the fluid flow so that fluid-elastic coupling does not occur. However, a certain low level of flow-induced vibration is to be anticipated in the as-built design.

However, after chemical cleaning, the tube and tube support plate geometry will have been changed. There are two possibilities for the post-cleaning configuration: (1) Tube and tube support plate clearances will be increased, with the tube support plate left intact; and (2) tube support plate sections may be missing, resulting in relatively large sections of unsupported tubes at various tube support plate locations. Increased vibrational displacement and possible changes in tube response frequencies could lead to increased amplitude fluid dynamic instabilities which would cause a coupling between fluid excitation and structural elastic response. Such a condition could lead to accelerated wear of tubes and tube support plates.

The objective, then, of this study was to evaluate the following:

- The structural change from the as-built stage to the post-cleaning stage as represented by the various test configurations to be studied.

- The system dynamic response, characterized by flow-induced vibrations and possible fluid-elastic coupling mechanisms, as addressed by the vibration flow tests.
- Tube fretting wear properties under steam generator environmental conditions for various combinations of tube and tube support plate material combinations as addressed by the accelerated tube wear tests.

The overlap between flow test results and mechanical vibration test results would provide for the direct correlation of test results on response, tube stress, and impact forces, and the overlap between analysis and test would provide a means of combined empirical and theoretical analysis.

7.2 Flow Induced Tube Vibration Test

The purpose of the vibration model tests was to identify and assess fluid dynamic forcing functions and flow-induced vibrations which may occur in critical regions of the steam generator. Regions considered were the entrance flow region and the U-bend region.

In the entrance flow region of the steam generator the tubes are exposed to the flow of secondary coolant as it enters the tube bundle through the downcomer inlet between the tube sheet and the lowest tube support plate. In this region, the straight tube sections in

the outer periphery regions of the tube bundle are subjected to high velocity, cross-flow water.

In the U-bend region of the steam generator the tubes are exposed to a complex, three-dimensional pattern of two-phase flow. Two subregions of interest are (a) the region of large radius U-bend tubes, and (b) the region of small radius U-bend tubes which are located along the interior centerline.

To acquire the necessary experimental data to facilitate an analysis of the nature and extent of flow-induced vibrations and the attendant effects of changing tube boundary conditions following chemical cleaning, the following test programs were identified. These test programs address the critical flow regions and tube structural configuration therein.

Test

- 1) Mechanical Vibration and Water Flow Test - Straight Tube Model
- 2) Two-Phase Flow Test - Large-Radius U-Bend Tube Model
- 3) Two-Phase Flow Test - Small Radius U-Bend Tube Model

The equipment designed for these tests is shown in Figures 7-1, 7-2, 7-3 and 7-4. Because of the early termination of this program, only the small radius U-bends were tested.

Figure 7-1
Detail Schematic of Straight Tube Model and Test Section:
Water Flow Test and Mechanical Vibration Test

Figure 7-2
Cross-Sectional Schematic of Tube Bundle Showing Tubes to be Instrumented.

Figure 7-3

Large Radius U-Bend Tube Model

Figure 7-4

Small Radius U-Bend Tube Model

Test Results

Tests on the small radius U-bend tube model were run on both "as-built" and "post-chemical cleaning" configurations.

Data analysis indicates the following trends:

- a) The vibration response of the small radius U-bend tubes to two-phase flow appears to exhibit forced vibration response characteristics rather than resonant coupling. The root mean square (RMS) acceleration levels, in general, are proportional to flow dynamic pressure, q , where:

$$q = \frac{1}{2} \rho U^2$$

and ρ = flow density

U = flow mean velocity.

For the test matrix, q was varied from approximately zero to 80 lb/ft². Flow conditions in the vicinity of the small radius U-bend tubes in the steam generator were predicted to be approximately 8 lb/ft³ density and 10 ft/sec velocity, corresponding to a dynamic pressure of $q = 12.4$ lb/ft². RMS acceleration levels at this condition ranged from approximately 0.15 g's at mid-span between the support plates (plates 5 and 6 in the steam generator) to approximately 0.6 g's out-of-plane vibration at the apex of the U-bends.

- b) Increasing tube support plate hole size from approximately 15 mils radial clearance to 40 mils radial clearance resulted in only minor changes in acceleration response levels.
- c) Acceleration response spectra are characterized by relatively pronounced resonant peaks in the 30 to 50 hertz range. Higher frequency response peaks occur in the 150 to 200 hertz range and in the 300 to 400 hertz range.

Assessment of flow instabilities attendant with the fluid supply and model support plate vibration indicate relatively low background levels such that measured tube vibration can be attributed directly to tube flow-induced disturbances.

7.4 Tube Fretting and Wear Test

Tube fretting wear properties under steam generator environmental conditions for various combinations of tube and tube support material combinations were addressed by the proposed accelerated tube wear test.

This test was designed to evaluate the Archard wear coefficient of various tube and tube support material combinations under environmental conditions approximating those in the steam generator. This test apparatus aimed to reproduce only those variables essential for

the establishment of the wear coefficient, that is water temperature, pressure and chemistry, and the materials of the tubes and wear plate. No attempt was made to reproduce the actual motion of the steam generator tubes. Wear would be imposed on the tubes using a small amplitude reciprocating motion introduced into the wear plate from an external drive system. Different material combinations would be achieved by testing tubes of two different materials (Inconel 600 and Incoloy 800). Wear variations would be achieved by using inserts made from four different materials (carbon steel, stainless steel, Inconel 600, and Incoloy 800). Tests would be performed a minimum of 100 million cycles, with samples removed at approximately 25 million cycles for analysis to establish wear characteristics and trends.

Test results from the accelerated wear tests would lead to characterization of tube wear for various combinations of tube and support plate materials. Analyses would consist of:

- o Inspection and measurement of the volume of wear for individual tubes which, when assessed in terms of material properties and work done on the tubes, could lead to a definition of the Archard wear coefficient.

- Analyses of tube life as evaluated from (a) the wear coefficient from tube wear tests, and (b) the work done associated with flow-induced tube vibration and tube impact upon the support plates.

The equipment designed and the wear test set-up is shown in Figures 7-9 and 7-10.

Figure 7-5

Accelerated Wear Test Machine

Figure 7-6

Schematic of Accelerated Tube Wear Test Set-up

The total exposure of personnel to radiation for preparation of openings in the steam generator and removal of the tube/support plate sample was 40.5 man rem. Exposure was held this low by the extensive use of lead shielding wherever feasible, and by locating control equipment in low radiation areas.

It has been demonstrated that the EDTA/citric solvent listed in Table 5-3 can effectively dissolve natural ("in-situ" formed) sludge and corrosion products in the annulus between a tube and support plate segment taken from a modern steam generator. Flow of solvent is necessary to achieve dissolution in a reasonable length of time, but corrosion rates of steam generator materials increase as solvent velocity increases.

Independent chemical cleaning tests performed by Babcock & Wilcox as part of the Utilities/EPRI Steam Generator Owners Group Program confirmed that the EDTA/citric solvent listed in Table 5-3 can clean corroded tube/support plate annuli in pot boilers designed to simulate modern steam generators. Details of the test and results will be given in an EPRI/Steam Generator Owners Group report to be published in 1980.

It is recommended that the EDTA/citric solvent developed in this work (Ref. Table 5-3) be used as a basis for developing a solvent for use in cleaning steam generators. However, before proceeding with actual cleaning of a given steam generator, it is recommended that, as a minimum, samples of sludge be removed from the steam generator and dissolution tests be run to ensure that the solvent developed is effective for the particular steam generator in question.

Furthermore, the following areas should be evaluated further:

1. Effect of solvent on welds, and heat affected zones of welds, of the materials of construction in the steam generators.
2. Effects of solvent velocity on dissolution of corrosion products and on corrosion of base metals.
3. Effect of solvent residuals on steam generator materials during post-cleaning operation.
4. Improved techniques for handling large volumes of low activity waste solvent and rinse waters.

APPENDIX A

REPORT ON SAMPLES
REMOVED FROM INDIAN POINT UNIT NO. 2
STEAM GENERATORS

BY

BATTELLE COLUMBUS LABORATORIES

FOR
CON EDISON

FINAL REPORT

on

INVESTIGATION OF SAMPLES RECEIVED FROM
INDIAN POINT UNIT NO. 2 STEAM GENERATOR

to

CONSOLIDATED EDISON COMPANY OF NEW YORK, INC.

July 13, 1979

by

J. H. Payer, J. L. White, and W. E. Berry

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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FINAL REPORT

on

INVESTIGATION OF SAMPLES RECEIVED FROM
INDIAN POINT UNIT NO. 2 STEAM GENERATOR

to

CONSOLIDATED EDISON COMPANY OF NEW YORK, INC.

from

BATTELLE
Columbus Laboratories

July 13, 1979

INTRODUCTION

This investigation was in support of Consolidated Edison Company of New York's program for PWR Steam Generator Secondary Side Chemical Cleaning in Indian Point Unit 2 Nuclear Plant. Battelle's Columbus Laboratories participated in the inspection of samples as the samples were removed from the Steam Generator. Selected samples were sent to Battelle for examination in support of the overall characterization effort. Objective of the investigation was to characterize the steel support plate, the corrosion products and deposits, and the Alloy 600 tubes.

A section of the first support plate above the tube sheet was removed from Steam Generator 23 of Indian Point Unit 2 Nuclear Plant. Eleven first and second row tube segments and their surrounding steel support plate structure were removed from the hot leg side of the steam generator. First row tube segments were approximately 4 inches long and second row tube segments were approximately 6 inches long. The support plate section nearly extended the full length along a flow slot and was approximately 14 inches long by 3 inches wide.

The samples were characterized by visual examination, metallography, scanning electron microscopy, electron microprobe, and X-ray diffraction. The investigation included

1.0 Characterization of Steel Support Plate

- 1.1 Dimensions
- 1.2 Profile of Corrosion
- 1.3 Morphology of Corrosion
- 1.4 Microstructure
- 1.5 Chemical analysis

2.0 Characterization of Corrosion Products/Deposits

- 2.1 Axial and Longitudinal Dimensions
- 2.2 Phase Identification
- 2.3 Elemental Analysis
- 2.4 Structure and Morphology

3.0 Characterization of Alloy 600 Tube

- 3.1 Dimensions
- 3.2 Profile of Corrosion
- 3.3 Morphology of Corrosion
- 3.4 Microstructure
- 3.5 Chemical Analysis.

Results of this investigation are in support of a program to develop a method for chemically cleaning the secondary side of steam generators.

RESULTS OF THE INVESTIGATION

An on-site examination of the steam generator samples was made at the Indian Point Nuclear Power Station. The steel support plate section did not remain intact during the removal operation, but rather it broke up into several pieces. Breaks occurred along tube hole to flow hole ligaments. First and second row tube stubs and pieces of the support plate were visually examined.

Two samples were sent to Battelle for examination: (a) an approximately 4-inch long, Alloy 600 tube segment and (b) a section of steel support plate. The support plate sample contained four fractured ligaments and two partial tube hole surfaces. Heavy corrosion product layers remained on the tube hole surfaces. Results of the examination of these samples are presented in this section. First, the steel support plate is characterized. Secondly, the corrosion products and deposits are characterized, and thirdly, the Alloy 600 tube is characterized.

Steel Support Plate Examination

The upper and lower surfaces of the support plate sample are shown in Figure 1. The photographs were taken on a line of sight parallel to the steam generator tubes. Ligaments are identified in Figure 2. The α and β surfaces were chosen arbitrarily because the upper and lower surfaces were not identified.

Thick deposits, approximately 1/16-inch, remained on both tube hole surfaces. Tube hole deposits were dense, hard, and brittle. Layers through the gray deposits were delineated along edges where deposits separated on removal from the steam generator. Flow hole deposits were black and not as thick as the tube hole deposits. In contrast to the dense tube hole deposits, these deposits were more amorphous and granular.

Shallow, general corrosion was observed on the α and β support plate surfaces. Without removal of corrosion products, the support plate thickness was 0.794 inches. Steel thickness between flow holes and between tube holes was measured with micrometers at locations near the α surface where no heavy deposits remained intact. The major "star" dimension, taken along a line connecting the centers of flow holes, was 0.54 inch. The nominal value for this dimension as specified in design drawings is 0.547 inch. The minor "star" dimension, taken along a line connecting the centers of tube holes, was 0.31 inch. The nominal value for this dimension is 0.344 inch.

1179 (a) α Surface

1182 (b) β Surface

FIGURE 1, UPPER AND LOWER SURFACES OF THE
STEEL SUPPORT PLATE SAMPLE

FIGURE 2. IDENTIFICATION OF LIGAMENTS ON THE STEEL SUPPORT PLATE SAMPLE

Tube hole surfaces are shown in Figure 3. The smooth, shiny deposits at mid-thickness of the support plate appear to have separated at the tube/deposit interface. Essentially, the full deposit thickness remained in these areas. Deposits near the upper and lower support plate surfaces had spalled and were not available for examination.

Corrosion products covered the broken ligament surfaces. This indicates that the ligaments were broken prior to sample removal, and the fractured surfaces were exposed to high temperature water. Ligament thickness measured on the as-received sample are presented in Table 1 along with nominal, typical and minimum dimensions determined from design drawings. The measurements were made with micrometers on the as-received sample. No heavy deposits remained at the locations where measurements were made.

The support plate specimen was cut along a line connecting flow hole centers, Section A-A on Figure 2. Piece A with Ligaments A and B was descaled in Clark's solution for examination of the extent and morphology of corrosion.

The descaled α and β surfaces are shown in Figure 4. Both surfaces exhibited shallow pitting and general corrosion. Several blunt tears on Ligament A at the α surface were observed. No other cracks or penetrations were observed.

The descaled tube hole surface is shown in Figure 5. A broad, shallow crater extended through the mid-thickness of the plate to within approximately 0.075 inch of the α and β surface. Depth of the corrosion crater was approximately 0.010 inch. Many small pits and several smaller craters were observed on the generally smooth surface. Outside of the larger crater, more surface roughness from scattered pitting was observed.

The fracture surface of Ligament A was examined with a Scanning Electron Microscope. Heavy corrosion after the ligament had broken left no distinctive features of the original fracture surface. A cross section through Ligament A at approximately 0.02 inch beneath the α surface is shown in Figure 6. Several penetrations are apparent along the tube hole surface. A photomicrograph of a penetration

1184 (a) Tube hole surface between
Ligaments C and D

1183 (b) Tube hole ligaments
between Ligaments A and B

FIGURE 3. TUBE HOLE DEPOSITS ON THE STEEL
SUPPORT PLATE SAMPLE

TABLE 1. LIGAMENT THICKNESSES MEASURED ON
AS-RECEIVED SUPPORT PLATE SAMPLE

	<u>Ligament Thickness (inch)</u>	
	α Surface	β Surface
Ligament A	0.09 ^(a)	0.06
Ligament B	0.06	0.06
Ligament C	0.07	0.07
Ligament D	0.07	0.07

(a) Nominal thickness = 0.084 inch

Typical thickness = 0.076 inch

Minimum thickness = 0.064 inch

6X

(a) α Surface

C-6015-004

6X

(b) β Surface

C-C015-004

FIGURE 4. UPPER AND LOWER STEEL SUPPORT PLATE SURFACES
AFTER DESCALING IN CLARK'S SOLUTION

6X

C-6015-005

FIGURE 5. DESCALED TUBE HOLE SURFACE
BETWEEN LIGAMENTS A AND B

20X

C-6015-006

FIGURE 6. LIGAMENT A APPROXIMATELY 0.02
INCH BENEATH THE α SURFACE

is shown in Figure 7. Orientation of the broad, blunt crack was not related to the steel microstructure.

Cross sections through Ligament A were examined at three levels through the support plate thickness: 0.02 inch beneath the α surface, 0.35 inch beneath the α surface, and 0.01 inch beneath the β surface. A montage across the broken ligament at 0.02 inch below the α surface is shown in Figure 8. Considerable deformation at the edges of the ligament is delineated by the elongated grains. It is likely that this deformation occurred when the remaining ligament thickness tore during fracture. The ligament thickness at fracture cannot be measured accurately because of the rounded edges on the fracture. The ligament at mid-thickness of the support plate (0.35 inch below the α surface) is shown in Figure 9. No grain elongation was observed along the irregular, fracture surface. Ligament A at 0.01 inch below the β surface is shown in Figure 10. As was observed mid-thickness, no grain elongation had occurred across the fracture surface.

Microstructure of the steel support plate was a typical ferrite/pearlite structure with equiaxed grains. No evidence of fissures or decarburization was observed. Spectrographic analysis of support plate sample determined its chemical composition in w/o to be 0.27 C, 0.53 Mn, 0.017 P, 0.031 S, 0.11 Cr, 0.17 Ni, 0.03 Mo, 0.23 Cu and less than 0.01 Si. The microstructure and composition are typical for steel specified for support plates in steam generators. The chemical composition is within the specification for ASTM specification A285C.

Deposits/Corrosion Products Examination

Deposit Structure and Morphology

Piece B with Ligaments C and D of the support plate specimen was mounted for metallographic examination of corrosion products and deposits. This piece contained approximately 180° of the tube hole surface between Ligaments C and D. A cross section through the deposits

200X

C-6015-007

FIGURE 7. BROAD, BLUNT CRACK IN LIGAMENT A
APPROXIMATELY 0.020 INCH BENEATH
THE α SURFACE - NITAL ETCH

150X

C-6015-008

FIGURE 8. CROSS SECTION OF LIGAMENT A AT 0.02 INCH
BELOW THE α SURFACE - NITAL ETCH

200X

C-6015-009

FIGURE 9. CROSS SECTION OF LIGAMENT A AT 0.35 INCH
BELOW THE α SURFACE - NITAL ETCH

125X

C-6015-010

FIGURE 10. CROSS SECTION OF LIGAMENT A AT 0.01 INCH
BELOW THE β SURFACE - NITAL ETCH

at 0.01 inch below the β surface is shown in Figure 11. The tube hole deposits, approximately 0.05 inch thick, were uniform around the circumference of the tube hole. With the exception of a deep penetration at Area 2, corrosion proceeded uniformly around the tube hole at this level in the support plate. The morphology of deposits at Areas 1 and 2 is described below.

A montage across the deposits at Area 2 is shown in Figure 13. This area includes a deep penetration into the steel. Similar to Area 1, a lamellar structure of the deposit similar to that at Area 1 was observed. A dense, gray inner layer was observed below a darker more heterogeneous outer layer. The outer layer contained fine particles of metallic copper. Extensive cracking of the brittle deposits was observed throughout the thickness, and a large crack appeared near the steel interface where the deposit spalled from the support plate. The tunnel-like penetration was broad and blunt. Deposits in the penetration were similar to those adjacent to the steel along the tube hole surface. Deposits 0.03 inch below the α surface were examined and they were similar to those near the β surface, however, no tunnel-like penetrations were observed.

Cross sections through the tube hole deposits at 0.34 and 0.40 inches below the α surface are shown in Figure 14. At both levels near the mid-thickness of the support plate, deposit thickness was considerably greater than near the upper and lower support plate surfaces. Deposit thickness ranged from approximately 0.20 to 0.14 inch around the circumference of the tube hole. A photomicrograph of deposits at 0.34 inch below the α surface is shown in Figure 15. A series of lamellar rings were clearly delineated. The steel/deposit interface was smooth with no evidence of localized corrosion. The deposits at mid-thickness were more homogeneous than those near the upper and lower surfaces. The dense, gray inner layer extended across approximately 90 percent of the deposit and was covered by a thin outer layer of dark, heterogeneous deposit. Extensive cracking of the deposit was observed. Circumferential bands of fine porosity were observed.

5X

C-6015-011

FIGURE 11. CROSS SECTION THROUGH DEPOSITS ON STEEL
SUPPORT PLATE AT 0.01 INCH BELOW THE β
SURFACE

Area 1 and Area 2 are delineated by
boxes.

130X

C-6015-012

FIGURE 12. A MONTAGE ACROSS THE TUBE HOLE DEPOSITS AT
AREA 1, 0.01 INCH BELOW THE β SURFACE

120X

C-6015-013

FIGURE 13. A MONTAGE ACROSS THE TUBE HOLE DEPOSITS AT
AREA 2, 0.01 INCH BELOW THE β SURFACE

5.25X

(a) 0.34-inch below the α surface

C-6015-014

5.25X

(b) 0.40-inch below the β surface

C-6015-014

FIGURE 14. CROSS SECTIONS THROUGH TUBE HOLE DEPOSITS AT MID-THICKNESS IN THE SUPPORT PLATE

Deposits

Steel

75X

C-6015-035

FIGURE 15. FULL THICKNESS OF DEPOSITS IN
A TUBE HOLE AT 0.34 INCH BELOW
THE α SURFACE

A longitudinal section through the tube hole deposit between Ligaments C and D is shown in Figure 16. Greater metal loss through the support plate mid-thickness was evident. The steel/deposit interface was smooth with no evidence of localized corrosion. The lamellar appearance and extensive cracking of the deposit were again observed.

Flow hole deposits were more granular than tube hole deposits. They were black and contained particles of metallic copper. Thickness was uniform through the support plate and ranged from 0.005 to 0.015 inches around the flow hole circumference.

Deposit Elemental Composition and Phase Identity

Scanning Electron Microscope/EDAX Analysis. A Scanning Electron Microscope (SEM) photomicrograph of tube hole deposits at 0.34 inch below the α surface is presented in Figure 17. The steel support plate is at the right. This area corresponds to the end of the deposit shown in the lower left corner of Figure 14a. The deposit composition was determined by X-ray dispersive analysis (EDAX) at Areas 1-a, 1-b, and 1-c as indicated by the arrows on Figure 17. Spot analysis was determined for Area 1-a at the locations shown in Figure 18. Results are reported in Table 2. At spot A on the steel substrate, Fe, Mn and a trace of Al were observed. At Spot B adjacent to the steel, lower levels of Fe and Mn and a trace of Al were observed. Oxygen is not detected by EDAX analysis. Analyses of other spots on this area indicate that the light gray, dense deposit is magnetite with only Fe and Mn detected. In cracks more heterogeneous material is observed. The heterogeneous material contains Fe, Si, Ca, S, Al, Mg, Zn, Ni and Cl. At Spot D on the round particle, Ni, Cr and Fe were observed indicating that the particle was Alloy 600. As shown in Figure 19, Area 1-b was taken along a wide crack in the deposit. Analysis of the debris in the crack found Fe, Cr, Zn, Ni, Mn and Al. Analyses on the dense deposit across the entire thickness found only Fe, Mn and a trace of Al.

8X

C-6015-015

FIGURE 16. LONGITUDINAL CROSS SECTION THROUGH THE TUBE
HOLE DEPOSIT BETWEEN LIGAMENTS C AND D

27X

C-6015-016

FIGURE 17. AREA ON THE TUBE HOLE DEPOSIT AT 0.34 INCH
BELOW THE α SURFACE FOR EDAX ANALYSIS

135X

C-6015-017

FIGURE 18. LOCATIONS OF EDAX ANALYSIS ON TUBE HOLE DEPOSITS AT AREA 1A ON FIGURE 16

TABLE 2. EDAX ELEMENTAL ANALYSIS OF TUBE HOLE
DEPOSITS AT 0.34 INCH BELOW
SURFACE

Element Concentration (K α Counts Above Background)													
Element Energy Level	Mg 1.26	Al 1.50	Si 1.75	P 2.01	S 2.31	Cl 2.62	Ca 3.69	Cr 5.40	Mn 5.89	Fe 6.40	Ni 7.47	Cu 8.03	Zn 8.63
Area 1A - Spot A	-	Tr ^(a)	-	-	-	-	-	-	364	11691	-	-	-
Area 1A - Spot B	-	Tr	-	-	-	-	-	-	103	9006	-	-	-
Area 1A - Spot C	-	82	-	-	-	-	-	-	147	8826	-	-	172
Area 1A - Spot D	-	Tr	Tr	-	-	-	-	2265	-	1004	6847	-	-
Area 1A - Spot E	180	485	1741	-	517	379	644	-	-	1237	123	-	679
Area 1A - Spot F	-	Tr	-	-	-	-	-	-	190	9283	-	-	Tr
Area 1A - Spot G	-	-	-	-	-	-	-	-	153	8734	-	-	41
Area 1A - Spot H	-	Tr	-	-	-	-	-	-	144	8618	-	-	-
Area 1B - Area A	-	52	-	-	-	-	-	-	101	3596	154	1954	174
Area 1C - Spot I	-	Tr	-	-	-	-	-	-	192	11920	-	-	-
Area 1C - Spot J	-	Tr	Tr	-	-	-	-	-	-	382	-	9262	-
Area 1C - Spot K	-	Tr	Tr	1728	-	-	168	-	616	5830	-	-	374
Area 1C - Spot L	68	Tr	1830	-	-	-	128	-	416	3796	-	-	116

(a) Tr = Trace

675X

C-6015-018

FIGURE 19. LOCATION OF AREA 1B EDAX ANALYSIS ON
TUBE HOLE DEPOSITS SHOWN IN FIGURE 16

The deposit remained homogeneous up to the outer layer where a more porous structure was observed. Analysis locations in this region, Area 1-c, are shown in Figure 20. Spot I is on the dense magnetite. Spot J on the light particles distributed in the porous layer next to the magnetite is rich in copper. At Spots K and L, in the porous layer, Fe, Mn, Si, P, Ca, Zn, Al and Mg were found.

Two areas on the longitudinal section through the tube hole deposits were analyzed by EDAX. Area 1 shown in Figure 21-a was near the α surface of the support plate. Locations of EDAX analysis are shown in Figure 21-b. The results are reported in Table 3. The dense deposit was magnetite and only Fe, Mn and traces of other elements were found. At cracks and regions of heterogeneous deposits Cr, Ni, Cl, Si, Al, S, Mg, and Zn were found in addition to Fe and Mn.

Area A-2 on the longitudinal section was at the mid-thickness of the support plate. The entire thickness of deposit at Area A-2 is shown in Figure 22-a. The outer layer of heterogeneous deposit is shown in Figure 22-b. Results of EDAX analysis at the locations indicated are presented in Table 3. Across the bulk of the deposit only Fe and Mn were detected with traces of other elements. The dense, homogeneous magnetite contained several fine cracks. At the thin outer layer many more elements were detected in addition to Fe and Mn, i.e., Zn, Cu, Ni, Ca, Cl, P, Si, Al. Traces of Cr were also observed.

Microprobe Analysis

Tube hole deposits were analyzed by electron microprobe. Three areas were analyzed: Area 1 and Area 2 at 0.01 inch below the β surface and an area on the longitudinal section through the deposits. Photographs of these areas were presented in Figures 12, 13, and 16, respectively. Results of these analyses are presented below.

A Back Scattered Electron (BSE) image of Area 1 and 0.01 inch below the β surface is shown in Figure 23-a. The three photographs cover the full deposit thickness from the steel substrate at the extreme left to the outer layer, closest to the tube, on the extreme right. The black

265X

C-6015-019

FIGURE 20. LOCATION OF EDAX ANALYSIS ON AREA 1C OF
TUBE HOLE DEPOSITS SHOWN IN FIGURE 16

23X

C-6015-020

(a) Tube hole deposits
near the α surface

233X

C-6015-020

(b) Locations for EDAX analysis

FIGURE 21. AREA 1 FOR EDAX ANALYSIS ON THE
LONGITUDINAL SECTION OF TUBE
HOLE DEPOSITS

TABLE 3. EDAX ELEMENTAL ANALYSIS OF TUBE HOLE
DEPOSITS ON THE LONGITUDINAL SECTION
OF THE SUPPORT PLATE

Element Concentration (K α Counts Above Background)													
Element Energy Level	Mg 1.26	Al 1.50	Si 1.75	P 2.01	S 2.31	Cl 2.62	Ca 3.69	Cn 5.40	Mn 5.89	Fe 6.40	Ni 7.47	Cu 8.03	Zn 8.63
Area 1 - Spot 1	-	Tr ^(a)	Tr	-	-	-	-	-	411	15431	-	-	-
Area 1 - Spot 2	-	Tr	Tr	-	146	-	-	-	251	9468	-	-	-
Area 1 - Spot 3	-	Tr	3474	-	-	-	-	-	1439	719	-	-	9971
Area 1 - Spot 4	692	2716	2707	-	121	261	-	-	1573	7008	711	601	2058
Area 1 - Spot 5	-	Tr	Tr	-	Tr	-	-	-	2201	23911	-	Tr	-
Area 2 - Spot 1	-	-	-	-	-	-	-	-	327	13069	-	-	-
Area 2 - Spot 2	-	-	-	-	-	-	-	-	318	12268	-	-	-
Area 2 - Spot 3	-	281	-	-	-	-	-	-	254	9037	-	-	-
Area 2 - Spot 4	-	Tr	Tr	-	-	-	-	-	164	9019	-	-	-
Area 2 - Spot 5	-	-	-	-	-	-	-	-	213	8985	-	-	-
Area 2 - Spot 6	-	79	Tr	-	-	-	-	Tr	212	9305	-	-	-
Area 2 - Spot 7	-	19	-	-	-	-	-	-	580	3253	-	-	-
Area 2 - Spot 8	-	-	-	-	-	-	-	-	126	9438	-	-	-
Area 2 - Spot 9	-	82	-	1931	-	66	51	-	481	4449	86	92	286
Area 2 - Spot 10	-	-	-	-	-	-	-	-	-	321	-	7904	-
Area 2 - Spot 11	-	-	-	2690	-	-	-	-	167	5014	203	-	206
Area 2 - Spot 12	-	257	-	2243	-	-	139	-	330	2599	125	-	117
Area 2 - Spot 13	-	306	4528	922	-	69	68	Tr	154	1150	87	-	81

(a) Tr = Trace

20X

C-6015-021

(a) Locations for EDAX analysis
across deposit

500X

C-6015-021

(b) Locations for EDAX analysis
at outer layer of deposit

FIGURE 22. AREA 2 FOR EDAX ANALYSIS ON THE LONGITUDINAL
SECTION OF TUBE HOLE DEPOSITS AT MID-THICKNESS
OF THE SUPPORT PLATE

FIGURE 23. MICROPROBE ANALYSIS FOR IRON, OXYGEN AND NICKEL AT AREA 1 ON DEPOSITS 0.01 INCH BELOW THE β SURFACE

band adjacent to the steel was a wide fissure parallel to the steel/deposit interface where the deposit apparently has separated. A distinct texture change at mid-thickness on the tube hole deposits is shown in the center image. Iron, oxygen, and nickel scans for each position also are shown in Figure 23. Iron intensity was greatest in the steel substrate, remained high and was uniform throughout the inner half of the deposit, and was non-uniformly distributed throughout the outer half of the deposit. Oxygen was more intense and uniformly distributed through the inner layer than the outer layer. Nickel was found throughout the outer layer and along the wide fissure in the deposit. Analysis for chromium detected few, small isolated spots of high chromium intensity in the outer layer, but no chromium above background levels was observed elsewhere.

X-ray images of manganese, sulfur, calcium and phosphorus are shown in Figure 24. Manganese was found at greater intensity in the outer layer than in the inner layer. Local areas of high manganese were observed along the fissure and at the interface between the inner and outer layers. Sulfur was non-uniformly distributed. High concentrations of sulfur were observed at the steel/deposit interface and at spots throughout the deposit. Calcium and phosphorus intensities exhibited a nearly exact one-to-one correspondence. Localized bands and islands of both were distributed throughout the outer layer. No intensities above background were observed in the inner layer except in the fissure where local, high intensity spots were observed.

The distributions of copper, zinc, aluminum and silicon in the deposit are shown in Figure 25. High intensity spots for copper were observed in the outer layer of deposit and along the fissure walls. The highest intensity spots correspond to metallic copper particles which were observed in the deposit; however, other areas of high copper concentration were observed in addition to the metallic copper particles. An intense band of zinc was observed along the side of the fissure, and local areas of high zinc intensity were found throughout the outer layer. Aluminum and silicon were observed in the outer layer and within the fissure, and intensities above background were observed in the inner layer.

FIGURE 24. MICROPROBE ANALYSIS FOR MANGANESE, SULFUR, CALCIUM, AND PHOSPHORUS AT AREA 1 ON DEPOSITS 0.01 INCH BELOW THE β SURFACE

FIGURE 25. MICROPROBE ANALYSIS FOR COPPER, ZINC, ALUMINUM, AND SILICON AT AREA 1 ON DEPOSITS 0.01 INCH BELOW THE β SURFACE

Magnesium and sodium were distributed throughout the outer layer of deposit and not detected in the inner layer. No chloride or carbon was observed above background intensity.

In summary, the microprobe results at Area 1 on the deposit at 0.01 inch below the β surface indicate two distinct layers in the deposit. The inner layer, adjacent to the steel, is homogeneous and only iron and oxygen were observed at high concentrations. In the outer layer of deposit and along the walls of a wide fissure in the inner layer, many other elements were detected. Iron, oxygen, copper, zinc, calcium, and phosphorus were distributed in patches throughout the outer layer. Nickel, manganese, aluminum, silicon, magnesium, and sodium were distributed more uniformly across the outer layer. Isolated spots of chromium were found in the outer layer. Sulfur was also detected at isolated spots and a band of sulfur was observed at the steel/deposit interface. No chloride or carbon was detected in the deposit.

A back scattered electron image of Area 2 at 0.01 inch below the β surface is shown in Figure 26-a. A photomicrograph of the same area was shown in Figure 13. The outer quarter of the deposit, at the extreme left in Figure 26-a, has a distinct texture compared to the inner three quarters of the deposit. Several wide fissures appear black in the photographs. These fissures are separations by the deposit. X-ray intensity images for iron, oxygen, and nickel are shown in Figure 26. The area analyzed extends from the outer edge of the deposit to near the deposit/steel interface. Iron was uniformly distributed through the inner deposit. The iron intensity was less and its distribution was non-uniform in the outer layer. Oxygen distribution was uniform throughout the deposit. Nickel intensity was greater in the outer layer and along the wide fissure near the steel/deposit interface.

X-ray intensity images for manganese, sulfur, calcium, and phosphorus are shown in Figure 27. A high intensity band of manganese was observed along the wall of a fissure in the inner layer of deposit. Concentration of manganese was greater in the outer layer. Sulfur occurred at distinct spots and was more intense in the outer layer. Calcium and phosphorus were found at the same sites in the outer layer.

FIGURE 26. MICROPROBE IMAGE AND ANALYSIS FOR IRON, OXYGEN AND NICKEL AT AREA 2 ON DEPOSITS AT 0.01 INCH BELOW THE β SURFACE

FIGURE 27. MICROPROBE ANALYSES FOR MANGANESE, SULFUR, CALCIUM AND PHOSPHORUS AT AREA 2 ON DEPOSITS AT 0.01 INCH BELOW THE β SURFACE

Both elements were also found as fissures in the inner layer, but neither element was detected in the bulk, inner layer deposit.

The distributions of copper, zinc, aluminum, and silicon are shown in Figure 28. Copper was detected as high intensity particles distributed non-uniformly in the outer layer and along the wide fissure in the inner layer. Zinc followed the same pattern as copper but was more uniformly distributed. Aluminum and silicon were detected in the outer layer and in fissures.

Magnesium and sodium were detected in the outer layer. A few discrete spots in the outer layer exhibited high intensity of chromium. No chloride or carbon was detected above background intensity levels.

The distribution of elements in the deposit at Area 1 and Area 2 are similar. Relative intensities for several elements in the outer and inner layers of Area 2 are presented in Table 4. Approximately twice the iron was found in the inner layer as was found in the outer layer. Nickel, copper and phosphorus were greater in the outer layer. Copper was detected in areas away from metallic copper particles. A trace of chloride was detected in the outer layer.

A tunnel-like penetration into the steel was observed beneath the deposit at Area 2. The tip of this penetration was analyzed for the distribution of elements. A back scattered electron image and the distributions of iron, chloride and sulfur are shown in Figure 29. The shape of the penetration was clearly delineated by lower iron, higher sulfur, and higher chloride intensities in the penetration than on the steel substrate. No intensity above background was detected at the penetration for nickel, phosphorus, copper, silicon, chromium, manganese, or zinc.

The distribution of elements was determined across the thick deposit on the longitudinal section shown in Figure 16. The area analyzed was at mid-thickness of the support plate. Microprobe images and X-ray intensities of iron, oxygen, and manganese at six positions across the deposit are shown in Figure 30. Position 1 covers the outer edge of the deposit which was adjacent to the Alloy 600 tube. A vertical feature in the deposit at position 3 and a fissure at position 4 were observed. The deposit/steel interface was included in position 6. Texture of the deposit

FIGURE 28. MICROPROBE ANALYSIS FOR COPPER, ZINC, ALUMINUM, AND SILICON AT AREA 2 ON DEPOSIT AT 0.01 INCH BELOW THE β SURFACE

TABLE 4. RELATIVE INTENSITIES FOR IRON, NICKEL,
CHLORIDE, PHOSPHORUS, AND COPPER AT
AREA 2 ON DEPOSITS 0.01 INCH BELOW
THE β SURFACE

	Outer Layer	Inner Layer	Steel Substrate
Iron	32.6% ^(a)	62.6%	98%
Nickel	2.3%	0.5%	--
Copper	1.7%	0.14%	--
Phosphorus	2.0%	n.d. ^(b)	--
Chloride	Tr ^(c)	n.d.	--

(a) Semi-Quantitative Analysis

(b) None Detected Above Background Intensity

(c) Trace < 0.003%

Tip of the Penetration

(a)

(b)

Iron

(c)

Sulfur

(d)

Chloride

FIGURE 29. MICROPROBE ANALYSIS OF THE TIP OF A PENETRATION INTO THE STEEL BENEATH THE DEPOSIT AT AREA 2

FIGURE 30. MICROPROBE ANALYSIS FOR IRON, OXYGEN, AND MANGANESE IN A TUBE HOLE DEPOSIT AT MID-THICKNESS OF THE SUPPORT PLATE

was uniform across its thickness to near the outer edge where a more heterogeneous deposit was observed. In general, the deposit composition was uniform over the thick, inner layer and varied sharply at the thin, outer layer. Iron concentration was greater in the inner layer than in the outer layer. Oxygen concentration was slightly higher and non-uniformly distributed in the outer layer. Manganese concentration was greater in the outer layer. A discontinuity in concentration was observed at position 4. Iron, oxygen, and manganese intensities were greater toward the outer edge. The composition change occurred along the vertical groove at position 4. Boron, sulfur and copper were observed along this groove. This is the only location where boron was detected. Boron concentration along the groove was approximately 1%.

Other elements that were detected in the outer layer were calcium, phosphorus, copper, nickel, zinc, sodium, magnesium, aluminum, silicon, and sulfur. The distributions of these elements at position 6, the outer edge of the deposit, are shown in Figure 31. With the exception of isolated spots of copper and sulfur, none of these elements was detected in the inner layer of deposit. No chromium, chloride, or carbon was detected in either layer of the tube hole deposit.

Microprobe analysis of the different areas of deposit are in good agreement. Two distinct layers were found. The inner layer, adjacent to the steel, is principally iron and oxygen with only trace amounts of other elements. The outer layer, which is closer to the Alloy 600 tube, is more heterogeneous and contains a large number of elements. The outer layer, which is closer to the Alloy 600 tube, is more heterogeneous and contains a large number of elements. At mid-thickness of the support plate, the outer layer is quite thin whereas, near the upper and lower support plate surfaces, the outer layer is thicker and comprises approximately half of the total deposit thickness. Evidence was found of a layered structure within the inner layer of deposit. Both fissures and concentration bands within the oxide and parallel to the steel interface were observed.

FIGURE 31. MICROPROBE ANALYSIS OF ELEMENTS AT THE OUTER EDGE OF TUBE HOLE DEPOSITS AT MID-THICKNESS OF THE SUPPORT PLATE

Chemical and X-Ray Diffraction Analyses

Scrapings of the dense, inner layer of deposits from mid-thickness of a tube hole in the steel support plate were analyzed for chemical composition and phase structure. Results of chemical analysis by optical emission spectroscopy, atomic absorption, and X-ray fluorescence techniques are presented in Table 5. The deposit was primarily iron. Small concentrations between 0.1 and 1.0% were detected for phosphorus, copper, silicon, nickel, zinc, sodium, and chloride. The only compound detected by X-ray diffraction technique was magnetite (Fe_3O_4). No lines were observed on the diffraction pattern which correspond to either copper or copper oxides.

Alloy 600 Tube Examination

The as-received Alloy 600 tube segment is shown in Figure 32. The tube contact area with the support plate was clearly delineated by the pattern of deposits on the tube surface. Away from the support plate contact area the tube was covered with a uniform, thin, black deposit. Within the support plate contact area, the majority of deposits had spalled leaving only patches of deposits scattered around the tube circumference.

The tube was deformed into an elliptical shape by an apparent squeezing action at the support plate. Inside diameter and outside diameter measurements were taken along the tube length at four axial locations: 0° , 45° , 90° , and 135° . In the photographs, the "N" marking is 270° , the protuberance is at 90° , and 0° is to the right on Figure 32-a. Measurements taken before and after the tube was descaled are presented in Table 6. Maximum deformation to an elliptical shape occurred at mid-thickness of the support plate, where the minor and major inside diameter axes were 0.726 inches at 0° and 0.796 at 90° , respectively. Away from the support plate the tube inside diameter was 0.770 inches. The elliptical deformation extended for more than 1-inch above and below the support plate contact area.

TABLE 5. CHEMICAL ANALYSIS OF TUBE HOLE DEPOSITS

Element	Concentration		
	% Metal ^(a)	% Metal ^(b)	% Metal ^(c)
Ba	<0.01		
B	0.05		
Si	0.2		
Mg	0.02		
Pb	0.02		
Cr	0.04		
Sn	0.01		
Ni	0.2		
Al	0.04		
Mo	0.02		
Cu	0.8	1.36	
Ag	<0.01		
Zn	0.5		
Na	0.2	0.11	
Ti	<0.01		
Ca	0.05		
Fe	Major	66.1	
Mn	0.2		
P			1.0
S			0.05
Cl			0.15

(a) Optical Emission Spectroscopy

(b) Atomic Absorption

(c) X-Ray Fluorescence

(a) 270° Orientation

(b) 90° Orientation

FIGURE 32. PHOTOGRAPHS OF THE AS-RECEIVED
ALLOY 600 TUBE SEGMENT

TABLE 6. INSIDE DIAMETER(ID) AND OUTSIDE DIAMETER(OD) MEASUREMENTS
FOR THE ALLOY 600 TUBE SECTANT AT FOUR AXIAL ORIENTATIONS

Elevation(ID)	OD Prior to Descaling(ID)				ID Prior to Descaling(ID)				ID After Descaling(ID)				Elevation(ID)
	0-180°	45-225°	90-270°	135-315°	0-180°	45-225°	90-270°	135-315°	0-180°	45-225°	90-270°	135-315°	
1/8"					.7652	.7661	.7730	.7675					1/8"
1/4"	.763	.770	.781	.769	.7635	.7700	.7739	.7700	.875	.886	.898	.885	1/4"
3/8"					.7618	.7694	.7812	.7640					3/8"
1/2"	.756	.768	.786	.766	.7614	.7700	.7833	.7651	.870	.884	.901	.882	1/2"
5/8"					.7571	.7714	.7837	.7647					5/8"
3/4"	.749	.769	.793	.764	.7541	.7711	.7861	.7590	.853	.880	.908	.872	3/4"
7/8"					.7466	.7582	.7465	.7528					7/8"
1"	.737	.763	.798	.758	.7410	.7664	.7985	.7650	.845	.879	.907	.869	1"
1-1/8"					.7312	.7681	.7961	.7416					1-1/8"
1-1/4"	.731	.761	.793	.752	.7295	.7643	.7960	.7355	.835	.879	.905	.872	1-1/4"
1-3/8"					.7314	.7595	.7964	.7370					1-3/8"
1-1/2"	.736	.762	.796	.752	.7264	.7635	.7955	.7325	.883	.875	.909	.865	1-1/2"
1-5/8"					.7292	.7567	.7956	.7407					1-5/8"
1-3/4"	.744	.770	.791	.760	.7420	.7510	.7394	.7590	.845	.875	.903	.869	1-3/4"
1-7/8"					.7340	.7600	.7315	.7500					1-7/8"
2"	.751	.773	.785	.765	.7405	.7511	.7730	.7602	.855	.875	.903	.875	2"
2-1/8"													2-1/8"
2-1/4"	.758	.772	.779	.768					.871	.880	.900	.879	2-1/4"
2-3/8"					.7550	.7611	.7793	.7770					2-3/8"
2-1/2"	.763	.770	.774	.769					.875	.883	.890	.879	2-1/2"
2-5/8"					.7643	.7670	.7792	.7711					2-5/8"
2-3/4"	.768	.770	.772	.770					.887	.883	.881	.878	2-3/4"
2-7/8"					.7685	.7693	.7723	.7712					2-7/8"
3"	.771	.769	.769	.771					.881	.884	.882	.881	3"
3-1/8"					.7704	.7710	.7710	.7700					3-1/8"
3-1/4"													3-1/4"
3-3/8"					.7713	.7687	.7661	.7662					3-3/8"

Prior to descaling the tube segment, scrapings of the deposits were taken from within the support plate contact area, at the edge of the support plate contact area, and away from the support plate contact area. In addition to these samples, scrapings were taken from the outside surfaces of two tubes from the hot leg of the second support plates. Results of EDAX elemental analyses of these samples are presented in Table 7.

Analyses of deposits at the contact area are similar to those for the outer layer of deposits on the steel support plate sample. Iron, nickel, and manganese are observed at significant levels. Chromium was found within the support plate contact deposit. Copper and zinc were found at significant levels within and away from the contact area. Calcium, phosphorus, magnesium and sodium were observed at the contact area only, whereas aluminum and silicon were observed in all deposits. No chloride was observed in any of the tube deposits. X-ray diffraction analysis of scrapings from the tubes between the first and second support plates found strong patterns for magnetite (Fe_3O_4) and copper (Cu), and strong/medium patterns for cuprite (Cu_2O) and tenorite (CuO), and a weak pattern for zincite (ZnO).

The Alloy 600 tube segment was descaled in an ammonium citrate (100 g/l solution and a sodium hydroxide (100 g/l) and potassium permanganate (30 g/l) solution. This solution left metallic copper deposited on the tube surface away from the contact area. Copper was removed by a 50 percent nitric acid solution. The descaled tube was split longitudinally along the 45-225° orientation. No evidence of defects or penetrations was observed on the inside diameter surface of the tube segment. The support plate contact area was clearly delineated on the outside diameter surface as shown in Figure 33.

Half-ring sections were cut from the tube segment at the N-end, mid-thickness and S-end of support plate contact area. Metallographic examination was carried out on the Alloy 600 tube at these three levels around the tube circumference from 45 to 225° on the side containing the "N" marking and the 315° orientation. Many shallow intergranular penetrations were observed along the outside diameter surface on the S-end

TABLE 7. EDAX ELEMENTAL ANALYSIS OF DEPOSITS
ON THE ALLOY 600 TUBE SEGMENT

Element Energy Level	Element Concentration (K α Counts Above Background)											
	Na 1.04	Mg 1.26	Al 1.50	Si 1.75	P 2.01	Ca 3.69	Cr 5.40	Mn 5.89	Fe 6.40	Ni 7.47	Cr 8.03	Zn 8.63
Within Contact Area	52	Tr ^(c)	139	1050	680	521	134	328	2332	830	118	213
Edge of Contact Area	170	104	121	548	338	509	-	486	2076	808	1044	1087
Away From Contact Area ^(a)	-	-	90	Tr	70	-	-	237	1771	860	1153	538
Away From Contact Area ^(b)	-	-	118	25	-	-	-	Tr	1218	262	1993	-

(a) From the tube segment specimen

(b) From second row hot leg tubes between the first and second support plate.

(c) Tr = trace

2.7X

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FIGURE 33. DESCALED ALLOY 600 TUBE SEGMENT
AT THE 270° ORIENTATION

sample. Less penetrations were observed at mid-thickness, and only a few were observed at the N-end. No inside diameter penetrations were observed. The matching piece of the tube from 45° to 225° containing the 135° orientation at the S-end of the contact area was examined. The extent of two axial locations where outside diameter penetrations were observed on the two S-end specimens are shown in Figure 34. These areas were from approximately 145° to 205° and from 310° through 0° to 15°. The penetrations were observed around the minor axis of the elliptical-shaped tube, i.e., where the tube had been squeezed.

Photomicrographs of the intergranular penetrations are shown in Figure 35. The branched penetrations were typically 1-2 mils deep, and the deepest penetration observed was approximately 3 mils. The penetrations were not observed at all grain boundaries by the affected area. The tube surface adjacent to the penetrations was smooth and exhibited no evidence of corrosion or any other form of damage.

The microstructure was typical for Alloy 600 steam generator tubes, and no evidence was observed of manufacturing or fabrication defects. Chemical analyses of the Alloy 600 tube segment was 0.05 C, 0.19 Mn, 0.003 S, 0.35 Si, 73.50 Ni, 18.35 Cr, 0.17 Cu, and 7.15 Fe. The carbon, chromium and copper concentrations are over the ASTM B-163 specified maximums of 0.15, 17.0 and 0.15, respectively. All other elements are within specification. Knoop hardness measurements with a 500 gram load were equivalent to R_b 67 hardness.

SUMMARY

Two samples removed from the Indian Point Unit No. 2 Nuclear Plant Steam Generator No. 23 were sent to Battelle's Columbus Division for examination: (1) a sample of steel support plate with corrosion product and deposits intact, and (2) an Alloy 600 tube segment from an area in contact with the tube support plate. The objective of the study was to characterize the steel support plate, the corrosion products and deposits, and the Alloy 600 tube. Results of the investigation are in support of a program to develop a method for chemically cleaning the secondary side of steam generators.

FIGURE 34. LOCATION OF O.D. PENETRATIONS ON ALLOY 600 TUBE SEGMENT AT THE S-END OF TUBE CONTACT AREA

500X

(a)

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500X

(b)

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FIGURE 35. INTERGRANULAR PENETRATIONS ALONG THE O.D. SURFACE OF THE ALLOY 600 TUBE SEGMENT WITHIN THE SUPPORT PLATE CONTACT AREA