THE WESTINGHOUSE STEAM GENERATOR SYMPOSIUM SUPPLEMENT #2

DECEMBER 1973

WESTINGHOUSE NUCLEAR ENERGY SYSTEMS

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INTRODUCTION

In March, 1973, Westinghouse presented the first Symposium on Steam Generator Experience for the nuclear power industry. This Symposium was conducted as part of a commitment to keep the industry informed on the latest developments in steam generator technology and operating experience. The proceedings of the Symposium were documented in a Symposium publication describing the steam generator experience acquired by Westinghouse and a discussion of the supporting technology.

In July, 1973, Supplement #1 to the Symposium book was issued to report on recent experiences gained through examinations at Beznau I and H. B. Robinson. This experience, in general, showed the effectiveness of the modifications in the phosphate chemistry program to prevent caustic stress corrosion.

A further briefing on steam generator experience was held in November, 1973 to present information on the 1973 steam generator inspections and ongoing steam generator programs. This report documents the information presented at the November briefing and is issued as Supplement #2 to the original Symposium publication.

SUMMARY

Westinghouse has 45 steam generators with Inconel tubes operating at 17 plants in the United States, Europe, and Japan Westinghouse has developed and collected substantial information on steam generator operation and maintainability and, as part of a commitment to keep the industry informed, is making this information available through formal presentations, meetings, and publications. This report contains the experience gained during the first ten months of 1973 as reported at the Steam Generator Briefing held during November, 1973.

The principle means of gathering information during this period was the eddy current testing of tubes in 17 steam generators at 7 plants and the removal of several tube sections for laboratory analysis. Experience with eddy current testing has shown it to be a reliable indicator of tube wall integrity and capable of detecting defects and characterizing these by location and magnitude. Laboratory examination of tube samples provides a direct visual observation of the tube wall condition after periods of inservice operation.

During 1971 and 1972 eddy current testing and the selective removal of steam generator tube sections identified a caustic stress corrosion phenomenon that occurred in several of the steam generators. Adjustments were initiated during 1972 in the secondary chemistry control program to prevent the development of caustic conditions within the steam generator. In those steam generators that had been eddy current tested before the implementation of the adjusted chemistry and then reinspected during 1973, there was a marked absence of the kind of eddy current test indications which were in the past attributed to caustic stress corrosion.

Thus the inspection programs conducted during 1973 have verified the effectiveness of the adjusted chemistry control program and have shown the caustic stress corrosion can be effectively eliminated by maintaining the recommended secondary side environment.

Eddy current testing of steam generator tubes at Connecticut Yankee, Zorita and San Onofre have detected indications of flaws at antivibration bar locations in the bend region. Examination of a tube sample removed from the bend region of San Onofre steam generator indicates that these flaws are the result of a fretting action between the tube and the adjacent antivibration support bar. The fretting is related to a round antivibration bar design used only in the earlier steam generators and appears to be self-limiting based on lack of observed growth in indications over a period of time. The round antivibration bar design has been replaced with a square Inconel bar design that is not susceptible to this phenomena.

Studies conducted by the R&D laboratories into the behavior of high temperature phosphates solutions along with some evidence gathered through eddy current testing and tube removal examinations indicate that plants

maintaining steam generator chemistry at a low sodium-to-phosphate molar ratio may experience wall thinning due to the development of localized acidic conditions. These studies have shown the existence of an invariant point at a Marcy-Halstead Na/PO_4 ratio of ~2.18. Below this point precipitation and concentration due to boiling can cause a shift to an even lower Na/PO_4 ratio and localized acidic conditions. Above this point, the solution pH is relatively unaffected by precipitation or concentration. Some limited observations of the occurrence of slight tube thinning in Westinghouse steam generators have been observed at two nuclear plants and are discussed

Westinghouse is recommending that plants be operated with a Marcy-Halstead sodium to phosphate ratio of 2.3 as a lower limit to provide margin and flexibility in operation while eliminating the possibility of localized acidic conditions.

In addition to eddy current test examinations and tube sample analysis, Westinghouse is conducting a number of research programs aimed at improving steam generator performance and maintainability. Some of the programs are discussed in the last section of this report.

A number of eddy current test inspections are planned for 1974. As more experience and information are collected, Westinghouse will make it available to the nuclear industry as part of our continuing program to keep the industry informed.

1

1973 STEAM GENERATOR INSPECTION

As part of a general surveillance program Westinghouse has conducted a large number of steam generator inspections during 1973. The purpose of these programs was to provide support for our customers in acquiring and analyzing information on steam generator experience and to determine the effect of chemistry control changes which have been implemented in steam generator operation. These programs consisted of in-the-field eddy current testing and the laboratory examination of tube segments removed from operating units. The examinations made at various plants and the conclusions reached from these investigations are discussed below.

H. B. ROBINSON AND BEZNAU I

H. B. Robinson and Beznau I plants were inspected during April and May of 1973 and their inspection results are reported in Supplement #1. Therefore, only a summary of these investigation results is presented here.

Table 1-1 lists the eddy current test inspections conducted at these two plants. Of the two indications found at Robinson, one was previously known to have existed and the other was in a region not previously inspected. At Beznau I, two indications were known to have existed previously, two were in a region not previously inspected, and the remaining four were in a region that had previously experienced a high caustic attack. The important result is that the indications that were known to have existed previously showed *no growth* in the extent of tube wall penetration. Also, it was clear from these inspections that the occurence of caustic corrosion that had been experienced earlier in these plants was no

TABLE 1-1
EDDY CURRENT INSPECTIONS AT H. B. ROBINSON AND BEZNAU I
APRIL-MAY 1973

Plant	Steam Generator	No. of Tubes Inspected	Region Inspected	No. of Eddy Current Indications	Location of Eddy Current Indications
H. B. Robinson	A	3200	Inlet	2	Above Tubesheet
	B	3200	Inlet	0	—
	C	3200	Inlet	0	—
Beznau I	A	1840	Inlet	1	Above Tubesheet
		1840	Bend	0	—
	B	1762	Inlet	7	Above Tubesheet
		1762	Bend	0	—

longer evident after the modified steam generator chemistry controls were instituted during 1972.

SAN ONOFRE

The San Onofre plant has not shown any evidence of the caustic corrosion problems that had been experienced at other Westinghouse plants. There had been two previous, separate steam generator occurrences which are noteworthy:

1. A small number of tubes were found to be constricted at the tube support plates.

2. A number of eddy current indications were found at antivibration bar locations.

The tubes constricted at the tube support plates are few in number and located on the outer periphery of the tube bundle. A discussion of this is presented in the Steam Generator Symposium publication.

The second occurrence was first noticed in July, 1972 during an outage in which eddy current testing revealed 23 indications of tube wall penetration in the bend region of "C" steam generator. Plans were made at that time to conduct a more thorough eddy current examination of the San Onofre steam generators and to remove a tube section in the bend region at the next refueling shutdown. During the June, 1973 maintenance-refueling outage, these tasks were accomplished. The results

TABLE 1-2
EDDY CURRENT INSPECTIONS AT SAN ONOFRE
JUNE 1973

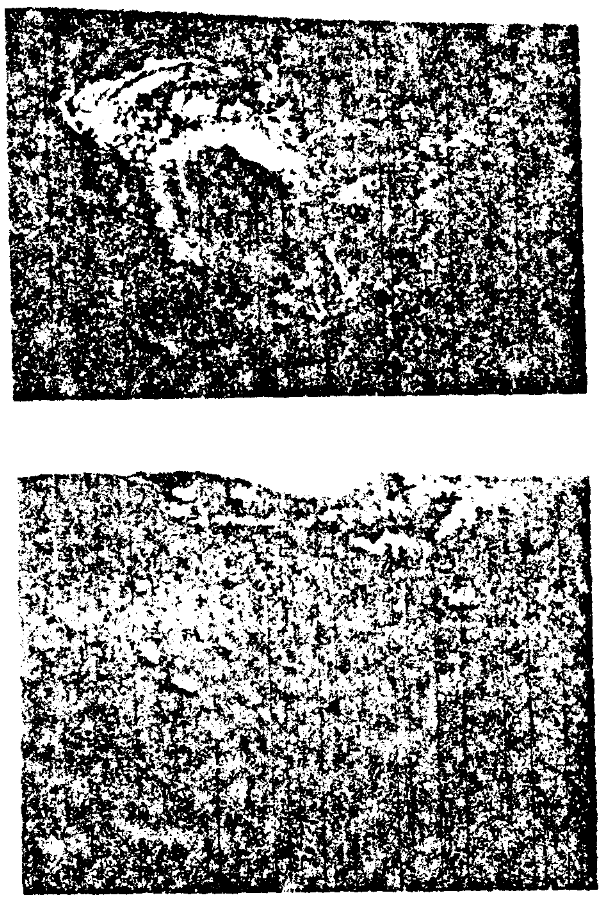
Steam Generators	No. of Tubes Inspected	Region Inspected	No. of Eddy Current Test Indications	Location Of Indication
A	2699	Inlet	0	--
		Bend	18	At antivibration bar
	1157	Outlet	15	1"-3" above tube sheet
B	876	Inlet	0	—
		Bend	92	At antivibration bar
	396	Outlet	0	—
C	772	Inlet	0	—
		Bend	61	At antivibration bar
	352	Outlet	0	—

of the eddy current examinations are listed in Table 1-2.

The table shows that a total of 171 bend region indications were found by eddy current testing. All these indications were adjacent to antivibration bar locations and most showed only slight tube wall penetration. Table 1-2 also shows that there were indications of tube wall penetration on the cold leg close to the tube sheet. Tube sections from the bend region and from the hot and cold leg region were removed and examined at the Westinghouse Research and Development Laboratories.

Laboratory Examinations of Bend Region Tube Section

Figures 1-1 and 1-2 show a photograph of the bend region defect found on the tube surface and the location in the steam generator antivibration bar region from which the tube sample was removed. Detailed examination of the tube segment showed that the defect was located on the tube at the contact point of the antivibration support bar and that the shape of the defect was a very close fit to the contour of the antivibration bar. There was



Damaged Area at Anti-Vibration Bar

Figure 1-1

San Onofre Tube Sample

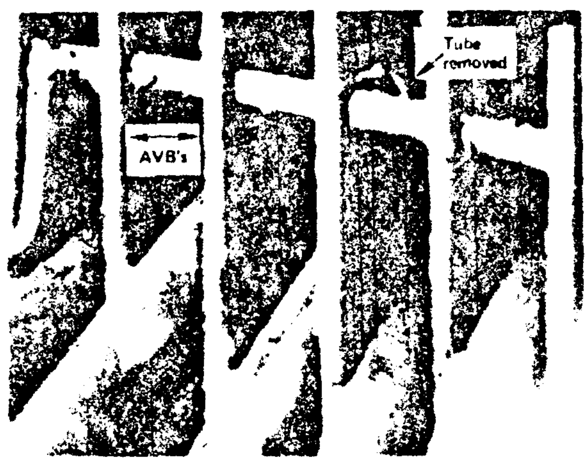


Figure 1-2

Location of Tube Removal in the Bend Region at San Onofre no evidence of any significant chemical or corrosive attack. Examination by steam generator manufacturing personnel showed that the antivibration support structure was not as tightly installed as they are in present day units. The conclusion reached through the various investigations was that the defect resulted from fretting in the form of low amplitude vibratory rubbing at the point of contact of the tube and antivibration bar.

A comparison of inspection results was made for 6 tubes that had been inspected at San Onofre in July 1972 and reinspected in June 1973. The 1973 inspection of these tubes shows that the indications of tube wall penetration had not increased significantly during the interim year of operation. This result suggests a self-limiting nature to the fretting being experienced. Apparently, as the antivibration bar wears the tube surface, the contact area increases thus reducing the contact force and the potential for fretting.

A further conclusion drawn from the San Onofre experience was that the fretting was related to the particular type of antivibration bar support design used in the steam generator. The antivibration support bars used at San Onofre are round; the round bar against a round tube provides a point contact which increases the potential for fretting because of the small contact area. Table 1-3 shows the types of antivibration support bar designs used in Westinghouse steam generators.

Westinghouse began using a square Inconel antivibration support bar design with all steam generators manufactured after the units built

TABLE 1-3
ANTIVIBRATION BAR DESIGNS USED IN WESTINGHOUSE STEAM GENERATORS

Plants	Design
San Onofre Connecticut Yankee Zorita	Round Carbon Steel Bars
Beznau I Beznau II	Round Inconel Bars
All other plants	Square Inconel Bars

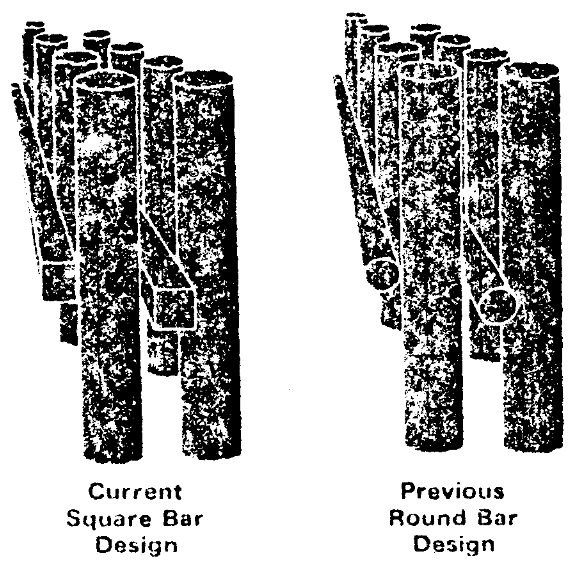


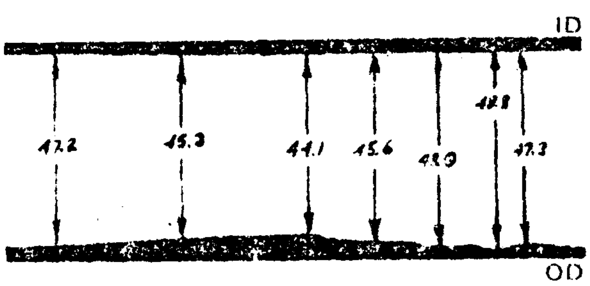
Figure 1-3
Comparison of Antivibration Bar Designs

for Beznau I and II. The square support bar design is compared to the round bar design in Figure 1-3. Use of the square bar provides for a larger surface contact area between the bar and the tube and thus minimizes the potential for fretting.

As mentioned, Connecticut Yankee and Zorita steam generators have similar antivibration bar designs and have also shown evidence of bend region defects. Beznau I and Beznau II steam generators which also use a round antivibration bar design have not shown any evidence of fretting. No evidence of this phenomena has been found in any of the steam generators using the square Inconel bar design.

Laboratory Examinations of the Cold Leg Tube Section

The tube segment removed from the cold leg of the "A" steam generator at San Onofre revealed a small defect which is characterized as localized thinning of the tube wall over a small area. The maximum depth of the tube wall depletion was about 7 mils. A photomicrograph of the defect is presented in Figure 1-4.



Cold-Leg Longitudinal Micro at Thinnest Point
Tube Wall Thicknesses in Mils

Figure 1-4
San Onofre Tube Sample

An investigation was begun to determine if the defect could have been induced during the final grinding and polishing operations at the tube manufacturing plant. Examination of the tube surface revealed the expected grinding marks, but none in the adjacent thinned areas. This suggested chemical attack as the mechanism of thinning.

Detailed analysis showed that no intergranular cracking had taken place indicating that concentrated caustic was not a likely source of the wall thinning. A study of the deposits found on the affected portion of the tube surface did not produce a definite cause for the defect. Based upon all the test data and observations, it was concluded that the type of defect experienced on the San Onofre cold leg was similar to what would be expected from a very localized chemical attack, but the specific cause of the tube wall thinning could not be determined by laboratory examination and analysis. The hot leg tube sample examined by the Westinghouse R & D Labs showed no evidence of thinning, pitting, or stress corrosion cracking.

BEZNAU II

A steam generator inspection program was conducted at Beznau II in August, 1973. The program consisted of eddy current inspection of both steam generators and removal of two tube sections from the inlet side for laboratory examination. One of the tube sections was examined in Europe. The other was sent to the Westinghouse Research and Development Center for analysis.

Although the field eddy current test results at the site failed to uncover any evidence of tube deterioration, the tube sample received by Westinghouse and the one examined in Europe showed slight thinning and pitting at a small area just above the tube sheet. This prompted a laboratory review of the eddy current test tapes which showed 10 tubes (including the two tubes which were removed) as having a small amount of thinning. In all cases the thinning was less than 20% of the tube wall and made discernible only through the reduction of background noise in the laboratory review of the eddy current tapes. The results of the eddy current test at Beznau II are reported in Table 1-4.

Laboratory Examination of the Beznau II Tube Sample

The Westinghouse Research and Development Center analyzed the tube sample by means

TABLE 1-4
EDDY CURRENT INSPECTIONS AT BEZNAU II
AUGUST 1973

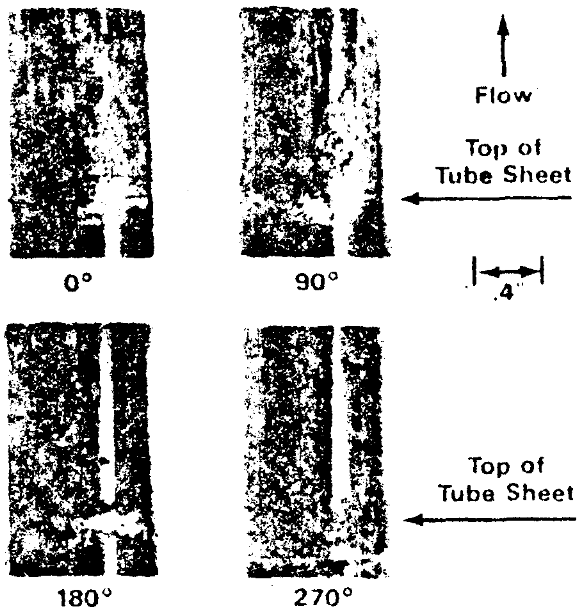
At the Site Test Results

Steam Generator	No. of Tubes Inspected	Region Inspected	No. of Indications
A	1453	Inlet	0
	50	Bend	0
B	1425	Inlet	0
	205	Bend	0

Laboratory Review of Eddy Current Test Tapes

Steam Generator	No. of Tubes Reviewed	Region Inspected	No. of Indications
A	350	Inlet	4
B	150	Inlet	6*

*Including the two tube sections removed for laboratory examination.



0° Location is Arbitrary

Figure 1-5
Beznau II Tube Sample

of a number of tests to characterize the tube wall depletion and to ascertain if possible its specific cause. Figure 1-5 is a view of the tube section as received showing the location of the depletion.

The affected area of the tube is characterized by having a number of pits and a small region of general thinning. These pits are very shallow having a maximum depth of 2.5 mils. The thinned region showed a maximum tube wall depletion of 4.6 mils or about 8% of the tube wall thickness.

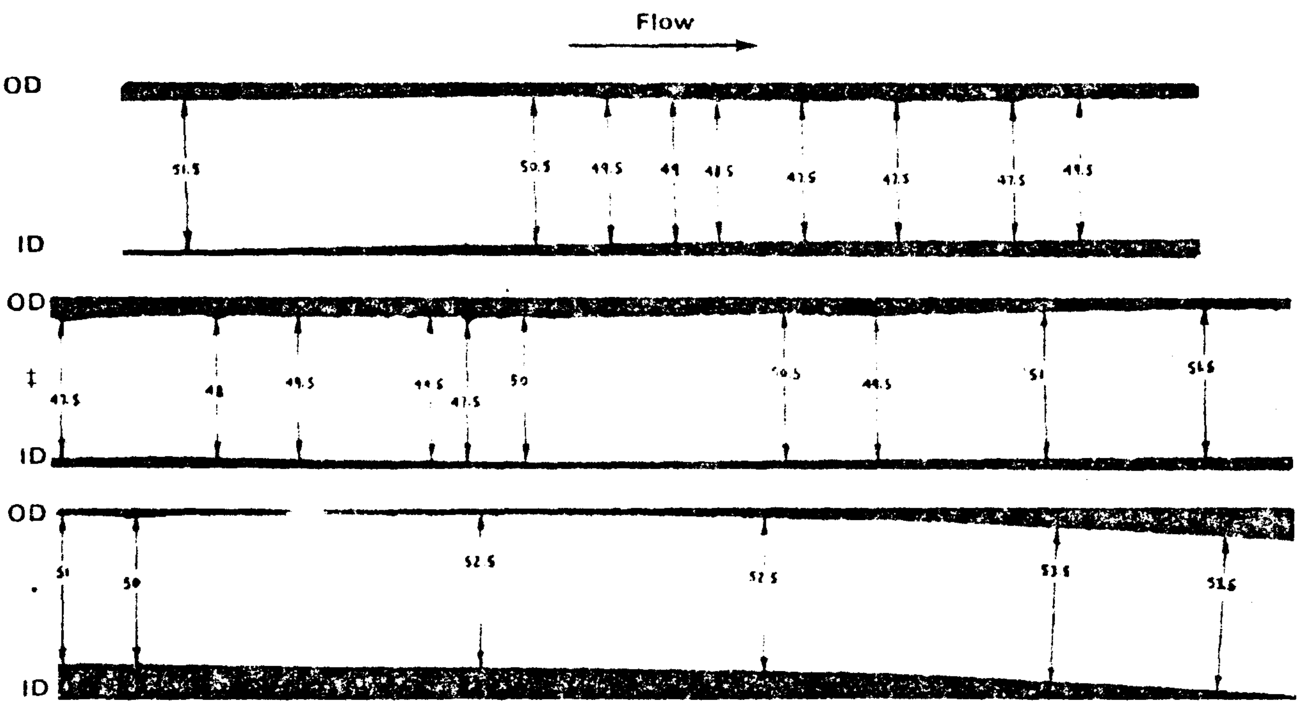
Figure 1-6 is a view of the tube wall at the affected region. Metallographic studies of the affected tube wall have shown that there is no evidence of intergranular attack. This indicates that concentrated caustic was not a likely contributor to the tube wall deterioration. Analysis of surface deposits through electron beam microanalysis did not show evidence of an aggressive environment that might have caused the wall thinning.

The laboratory analyses were unable to pinpoint a definitive cause for the tube surface depletion. The conclusion reached was that the defect was probably caused by a localized chemical condition, possibly an acid environment. A following section of this report on phosphate chemistry solutions discusses a potential mechanism whereby a localized acid condition could exist.

CONNECTICUT YANKEE

Connecticut Yankee was shut down for refueling and turbine maintenance and repair during July-October 1973. This plant shutdown was used to conduct extensive eddy current testing of the four steam generators. The results of this testing are reported in Table 1-5.

The table shows that there are 38 indications of tube wall penetration on the hot leg close to the tube sheet. These indications are very similar in location and eddy current test characterization to the caustic stress corrosion indication previously found at other plants. This was not an unexpected observation since caustic corrosion indications were previously found in the number 3 steam generator and



Wall Thickness in Mils

Figure 1-6
Beznau II Tube Sample

the other three steam generators had not previously been extensively inspected.

Of particular interest is the fact that no hot leg indications were found in the No. 3 steam generator. This is important because the No. 3 steam generator was the only steam generator at Connecticut Yankee to have previous eddy current test data and, therefore, the only reference for comparison to determine the effectiveness of the modified chemistry specifications. The previous inspections occurred in 1972 and consisted of examining the inlet portions of 1500 tubes in the No. 3 steam generator by eddy current testing. A total of 14 indications of tube wall penetration were found at that time and these tubes were plugged.

Table 1-5 also indicates that 71 eddy current test indications were found in the bend region at the antivibration support bar locations in the Connecticut Yankee steam generators. These eddy current test results are indicative

TABLE 1-5
EDDY CURRENT INSPECTIONS AT CONNECTICUT YANKEE
JULY-OCTOBER 1973

Steam Generator No.	No. of Tubes Inspected	Region Inspected	No. of Indications Found	Location of Indications
1	1493	Inlet	5	Above Tubesheet
	432	Bend	40	At Antivibration Bar
2	1605	Inlet	25	Above Tubesheet
	536	Bend	13	At Antivibration Bar
3	892	Inlet	0	—
	342	Bend	6	At Antivibration Bar
4	2255	Inlet	8	Above Tubesheet
	625	Bend	11	At Antivibration Bar
	Representative Sample	Outlet	0	—

of a similar type of fretting phenomena to that experienced at San Onofre. As mentioned earlier, Connecticut Yankee and San Onofre have the same round carbon steel antivibration support bar design.

These fretting indications show only a small penetration into the tube wall. Plans are being made to reinspect the Connecticut Yankee steam generators in 1974 to further confirm the self-limiting characteristic of the fretting process.

ZORITA

Eddy current tests inspections were made in the steam generator at Zorita during October, 1973. The results of these tests are reported in Table 1-6.

The steam generator at Zorita has the same antivibration support structure with round bars as was used in the steam generators at Connecticut Yankee and San Onofre. As such, it has the potential for developing the same type of fretting defects experienced at those plants. The defect indications at Zorita are small and will be monitored during future steam generator inspections.

MIHAMA 1

A reinspection of the Mihama 1 steam generators in March-April 1973 after operation

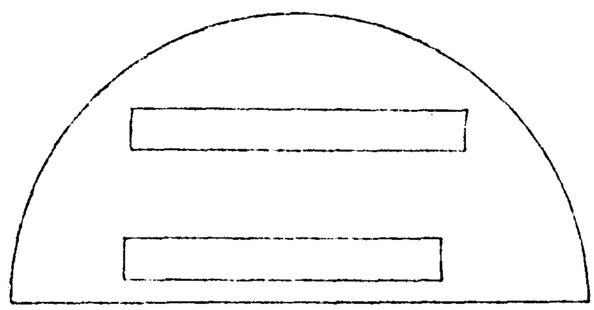
TABLE 1-6
EDDY CURRENT INSPECTIONS OF ZORITA
OCTOBER 1973

No. of Tubes Inspected	Region Inspected	No. of Indications	Location of Indications
2200	Inlet	3	1-3" above tubesheet
900	Bend	32	At antivibration bars

for several months at reduced power showed that the tube wall thinning in the bend-support strap region had increased and that more steam generator tubes had been affected. These steam generators were designed and manufactured by Combustion Engineering. Differences between the Combustion Engineering and Westinghouse design were described in the Steam Generator Symposium Book.

The Combustion Engineering design uses 4" wide carbon steel straps to maintain tube bundle rigidity. All of the indications of tube defect have occurred at locations where the carbon steel straps intersect with a bend in the tubes. The indications are all located in two general regions of the steam generator tube bundle as outlined on the tube sheet plan view in Figure 1-7.

Detailed laboratory analysis of the tube samples removed during 1972 showed that the defects were not the result of fretting, but resulted from an erosion or corrosion process. The actual mechanism of the wall thinning has not been determined.



Hot Leg Plan View

Figure 1-7
General Area of Affected Tubes at Mihama

A majority of the tubes in the affected regions of the Mihama 1 steam generators have been plugged. The plant is still capable of 100% power operation although it is presently restricted to reduced power operation by the Japanese regulatory agency.

2 RESULTS OF LABORATORY STUDIES IN THE BEHAVIOR OF PHOSPHATE SOLUTIONS

Sodium phosphate has been employed throughout the world as an additive to steam boilers since the early days of the electric utility industry. Phosphates have been utilized in fossil boilers primarily for control and prevention of scale and resultant tube "burnout" and secondarily for control of boiler water chemistry to prevent corrosion. The use of sodium phosphate additives has been proven as an effective method of chemistry control through many years of boiler experience.

Formation of scale is not in itself as critical a problem in a saturated steam nuclear generator as in a fossil boiler. Prevention of corrosion has become the primary objective of nuclear steam generator chemistry control. Scale formation must still be avoided in nuclear steam generators insofar as tube scale can provide sites for localized concentration of non-volatile corrosive solutions.

Operating experience has proven that some condenser leakage will inevitably occur, resulting in the introduction of non-volatile impurities into the steam generator. The chemical makeup of condenser circulating water cannot generally be predicted because of upstream dumping, climatological changes and other perturbations. If steam generator chemistry is being controlled only by addition of volatile substances, then the chemical environment resulting from the introduction of non-volatile impurities is unknown (and uncontrolled). Thus even minor condenser leaks can adversely affect steam generator chemistry and require immediate correction.

For these reasons, phosphate chemistry has been used in nuclear steam generators since the beginning of the nuclear power industry. Phosphate chemistry when properly controlled, can effectively counteract the undesirable effects of non-volatile impurities and allow additional flexibility in plant operation during normally expected condenser leakage. Because of the importance of chemical conditions in nuclear steam generators, the study of the nature of phosphate chemistry at steam generator conditions and refinement of phosphate control parameters has been a continuing effort.

CHEMICAL CONCENTRATION EFFECTS IN STEAM GENERATORS

Concentration of non-volatile dissolved chemicals is inherent in the operation of any boiler whenever these chemicals are introduced to the boiler liquid. Steam generators have less than complete mixing of the liquid in all areas of the generator, so that the boiling mechanism can produce different chemical concentrations in different areas of the liquid phase in the steam generator. Formation of scale or sludge can produce low flow areas which allow further localized concentration of dissolved chemicals. One mechanical model which has been suggested to explain this concentration phenomenon is shown in Figure 2-1. The mechanism shown could allow evaporative concentration of steam generator non-volatile chemicals at or near the tube surface.

Concentration of dissolved chemicals in water solution generally elevates the boiling point

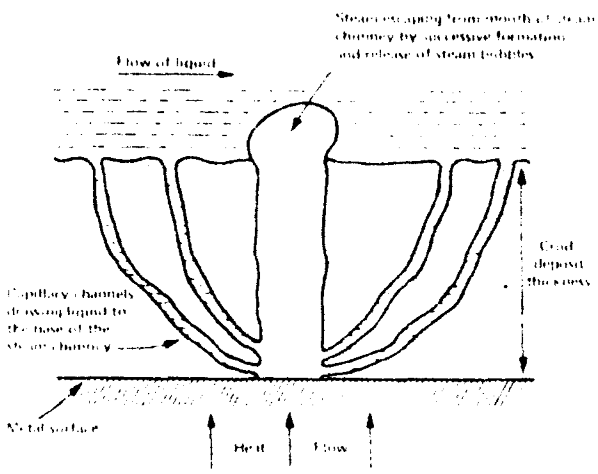


Figure 2 1
Model of Flow In Deposit

of the solution. Theoretically, localized concentration of the solution and resultant elevation of the boiling point in the steam generator can continue until the boiling point elevation is equal to the highest super-heat temperature available, which corresponds to the difference between the reactor coolant hot leg temperature and the saturation temperature in the steam generator. This phenomenon was discussed in Section 5 of the Westinghouse Steam Generator Symposium document.

Only unusually soluble materials, such as sodium hydroxide and some potassium salts, can be concentrated until the boiling point elevation equals the maximum superheat temperature available in a nuclear steam generator. Most salt solution mixtures will become saturated with one or more of the constituent solutes before the maximum boiling point elevation is reached. Precipitation then occurs and this precipitation in general causes a shift in the composition of the remaining solution. Thus, a prime objective of any steam generator chemistry control program must be to avoid chemical conditions which could produce an adverse change in solution composition upon concentration.

PHYSICAL CHEMISTRY OF SODIUM PHOSPHATE SOLUTIONS IN STEAM GENERATORS

The implications of the concentration, precipitation and localized change in composition of chemical solutions in the steam generator have warranted further investigation of these phenomena. Important aspects of this investigation are determination of the direction and magnitude of the shift in steam generator solution compositions resulting from local concentration effects, and determination of the concentration and composition of any solution remaining at the maximum superheat condition.

Sodium phosphate solutions utilized in steam generators are salt mixture solutions that are part of the ternary system Na_2O-P_2O_5-H_2O. In general, precipitation of a solid from a salt mixture solution in a ternary system will alter the composition of the remaining solution. Figure 2-2 illustrates on a typical isothermal diagram how the solution can be made richer in component A or component B, depending on the composition of the solution relative to the composition of the solid that precipitates from it. There will be no change in liquid composition only if (1) the solution composition is a "congruent composition," at which the equilibrium solid and solution happen to have the exact same composition; of if (2) the solution is at an "invariant point," at which two different solid phases are in equilibrium with the same solution phase. The existence of an invariant point is a thermodynamic requirement of Gibbs' phase rule as applied to equilibrium in heterogeneous systems.

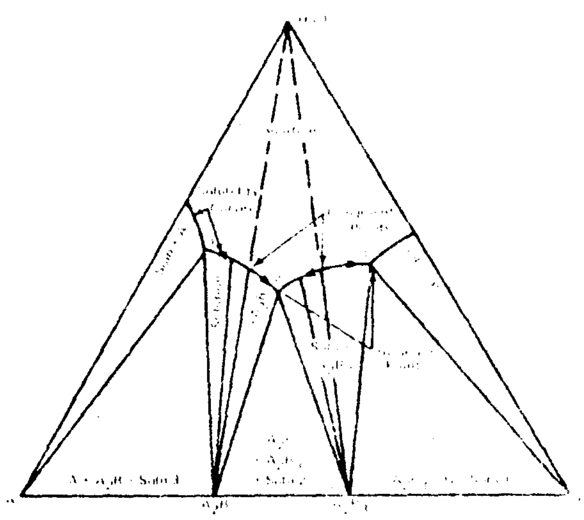


Figure 2-2
Isothermal Solubility Diagram

Congruent solution compositions are *unstable*, in the sense that a slight deviation of the solution either way from the exact congruent composition will initiate a progressive change away from the initial composition as water continues to be evaporated and solids precipitated. In contrast, invariant compositions are *stable*, since the solution will return to the invariant point if its composition is perturbed while the solution is being evaporated.

Figure 2-3 illustrates some of the special features that can occur in ternary systems, several of which are analogous to those observed in the sodium phosphate-water system at high temperatures. These are (1) a liquid phase hydroxide at the right hand terminus of the sequence of solubility curves; (2) intermediate solid phases that are a broken series of solid solutions rather than definite stoichiometric intermediate compounds; (3) coincidence of a congruent composition and an invariant point; and (4) an "incongruently saturating" solid phase.

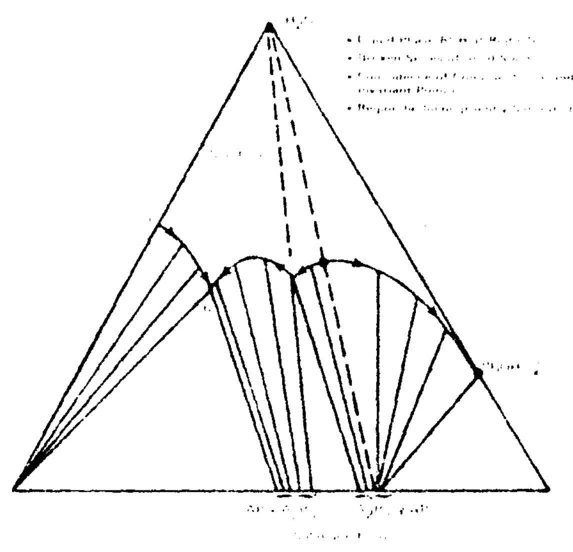


Figure 2-3
Isothermal Solubility Diagram
Solid Solutions Between Two Compounds

PREVIOUSLY AVAILABLE INFORMATION

Currently employed phosphate steam generator chemistry control programs are predicated on a large base of experimental and operational data. This data generally has shown phosphate solutions to have the following characteristics:

- The system Na_2O-P_2O_5-H_2O is complicated by many hydrate phases and numerous singular points at temperatures below 100°C. This system exhibits high solubilities and the solubilities of the various sodium salt constituents increase with temperatures up to 100°C.

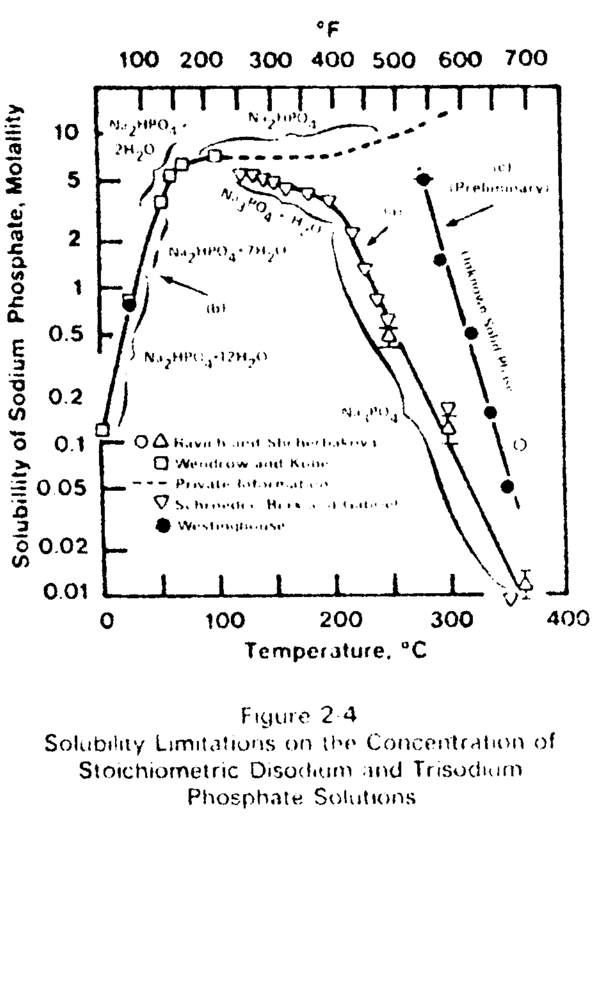


Figure 2-4
Solubility Limitations on the Concentration of Stoichiometric Disodium and Trisodium Phosphate Solutions

- Trisodium phosphate salts exhibit a sharp retrograde solubility with temperatures above 215°C. The solid phase produced by precipitation of solutions having a Na/PO_4 molar ratio of about 3 at high temperatures has a variable composition. At 300°C a congruent composition exists at a Na/PO_4 molar ratio of about 2.85; i.e., the solid precipitate will exhibit the same composition as the remaining solute. The solubility characteristics of trisodium phosphate are shown by curve (a) in Figure 2-4.

- Disodium phosphate salts exhibit an essentially constant solubility from about 100°C to 200°C. Disodium phosphate salts were reported to exhibit an increasing solubility with temperatures above about 200°C. These solubility characteristics are shown by curve (b) of Figure 2-4.

The retrograde solubility characteristic of trisodium phosphate has long been recognized as a major cause of hideout in operating steam generators. This retrograde solubility and the existence of a congruent point at a Na/PO_4 molar ratio of 2.85 is the basis for establishing an upper allowable limit on the Na/PO_4 molar ratio. The recommended congruent phosphate chemistry control program was discussed in greater detail in Section 5 of the Steam Generator Symposium document.

PRELIMINARY RESULTS OF WESTINGHOUSE RESEARCH

The Westinghouse Research and Development laboratories are investigating the characteristics of sodium phosphate solutions at various temperatures. One aspect of this investigation has been determination of the solubility limits of disodium phosphate solutions at high temperatures. This was accomplished by measuring change in electrical conductivity of various concentrations of Na_2HPO_4 solutions with increasing temperature. Data obtained from these experiments is shown in Figure 2-5. The conductivity decreases observed in these experiments indicate a solution concentration decrease caused by precipitation of some of the salts in solution. This retrograde solubility characteristic is shown by curve (c) of Figure 2-4.

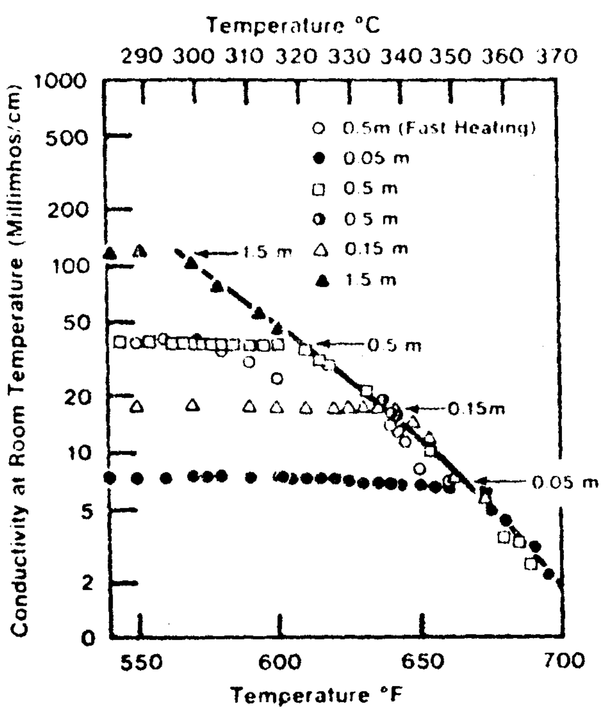


Figure 2-5
Conductivity Variations of Disodium Phosphate Solutions on Heating

Because this retrograde solubility characteristic differs radically from high temperature disodium phosphate solubility depicted by curve (b), the precipitating solid composition associated with curve (c) must be different from pure disodium phosphate. Attempts to recover and identify this precipitate have thus far been unsuccessful.

Composition of the liquid phases and precipitating solid phases in disodium phosphate solutions at high temperature was determined by measurement of the composition of the remaining solution. Analysis of solution samples revealed a decrease in the Na/PO_4 ratio and a decrease of pH for solutions with an initial Na/PO_4 molar ratio of 2.0. Typical data obtained from these experiments is shown in Table 2-1. From this data it is clear that a Na/PO_4 molar ratio of 2.0 is not a congruent composition.

Solutions of various initial concentrations and initial Na/PO_4 molar ratios above and below 2.0 were analyzed in a similar manner at about 300°C. Data obtained from these experiments is shown in Table 2-2.

The data in Tables 2-1 and 2-2 was analyzed to determine the sodium phosphate solution invariant point—the stable Na/PO_4 molar ratio which the solution assumed as precipitation progressed. This data indicates that solutions with initial Na/PO_4 molar ratio of 2.0 or less became more acid (Na/PO_4 ratio decreased) as precipitation progressed. Therefore, the invariant point must be above a Na/PO_4 ratio of 2.0

Further study of solutions with initial Na/PO_4 molar ratios around 2.2 to 2.3 indicated a stable molar ratio or invariant point of about 2.14 to 2.2, as precipitation progressed. Typical data is shown in Table 2-3.

TABLE 2-1
PRECIPITATION FROM 0.5 MOLAL SOLUTION INITIALLY Na/PO_4 2

Temp on Sampling (°F)	pH of Sample Diluted 5 Fold	m Moles PO_4 in 5 ml	Na/PO_4 in Soln.
100	9.08	2.41	2.00
205	9.02	2.43	2.00
310	9.00	2.43	2.00
400	8.88	2.45	1.98
495	8.46	2.42	1.97
555	8.23	2.38	1.95
600	7.98	1.29	1.86
640	7.80	0.76	1.83
645	7.73	0.54	1.87
660	7.51	0.20	1.75
660	6.59	0.015	1.4*
660	6.60	0.020	1.4*

*From pH and PO_4 Conc. Only

TABLE 2-2
COMPOSITIONS OF LIQUID AND SOLID PHASES IN EQUILIBRIUM AT 300 C

Solution Initial Na/PO_4 Ratio	Solution Na/PO_4 Ratio	Na/PO_4 Ratio for Solid Formed
1.5	1.47	1.76
1.7	1.66	1.81
2.0	1.86	2.16
2.0	1.96	2.11
2.19	2.15	2.32
2.21	2.17	2.29
2.31	2.22	2.74

TABLE 2-3
SOLUTION COMPOSITION VARIATION ON PRECIPITATION OF SOLIDS FROM SOLUTION INITIALLY CLOSE TO AND ABOVE INVARIANT POINT

Temperature Range (°F)	Percent Depletion of Dissolved Salt by Precipitation	Solution Na/PO_4 Ratio
532	0	2.21
570 590	14	2.17
595 607	29	2.16
612 627	56	2.15
630 640	75	2.14
649 667	89	2.14

The data of Table 2-2 is shown on a graph along with previously existing data in Figure 2-6. This figure indicates graphically the solution invariant composition. The previous data was discussed in Section 5 of the Steam Generator Symposium document.

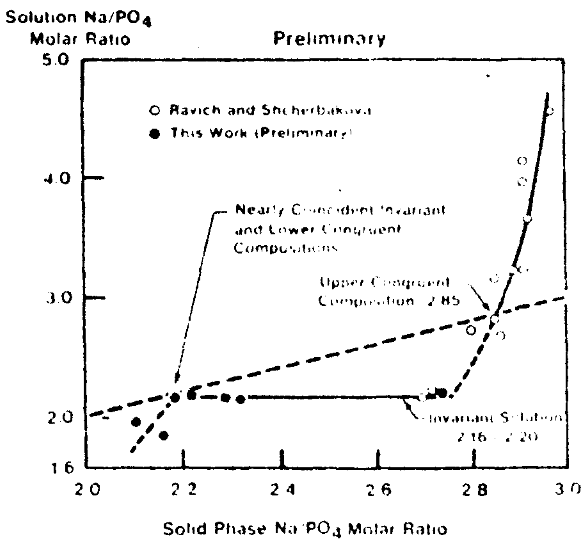


Figure 2.6
Compositions of Solid and Solution Phases in Equilibrium System Na_2HPO_4-NaOH-H_2O at 300 C (572 F)

PRELIMINARY CONCLUSIONS

Sodium phosphate solutions with an initial Na/PO_4 ratio above the invariant point (about 2.2) cannot shift to compositions with molar ratio lower than the invariant composition. Such a solution, when concentrated sufficiently will simply "dry up" at the invariant composition. Solutions with initial Na/PO_4 ratios less than the invariant composition will become more acid in composition as precipitation progresses, i.e., the solution Na/PO_4 ratio will progressively decrease. Because of the high solubilities at low Na/PO_4 ratios, no limiting effect on this shift to a lower pH has yet been identified.

Implementation of revised practices at operating Westinghouse plants in 1972 was aimed at maintenance of a low Na/PO_4 ratio and prevention of the formation of caustic. As a result, some plants have operated with a Na/PO_4 ratio at or below the invariant point. Conditions exist in operating steam generators which could allow the localized formation of acidic solutions if the bulk solution Na/PO_4 ratio is significantly below the invariant point. Analysis of occurrences of slight tube wall thinning, discussed in the first section of this supplement, indicates that this thinning may have been caused by such a localized acid condition.

Based on preliminary analysis of the phenomena discussed above, it seems prudent to modify the congruent phosphate chemistry control program. Thus a lower Marcy-Halstead Na/PO_4 control limit of about 2.3 is recommended, to maintain the solution above the invariant point and to preclude the possibility of localized acidic conditions. The upper limit of 2.6 molar ratio is retained, since the current studies reaffirm an upper congruent point of about 2.85.

3

ONGOING STEAM GENERATOR PROGRAMS

A continuing effort has been made by Westinghouse to investigate possible improvements in the steam generator design and in operating recommendations. Some of the programs which are part of this effort were discussed in the Steam Generator Symposium document. Additional operating data and theoretical information has warranted initiation of additional support programs. The major Westinghouse steam generator programs are summarized below.

NEAR TERM ACTIVITIES

Chemistry Technology

Investigation of steam generator chemistry technology is continuing with near term emphasis on the definition of the physical chemistry of sodium phosphate solutions. The solubilities of sodium phosphate solutions as a function of Na/PO_4 molar ratios and temperature are being studied to develop a phase diagram as a function of temperature for the system Na_2O-P_2O_5-H_2O. Investigation of reactions between phosphate and sludge are continuing with the aim of evaluating potential alkali and acid-forming chemical reactions.

Materials Technology

Corrosion tests of Inconel-600 tube materials at operating temperature and chemistry conditions are proceeding to determine the general corrosion rate as a function of temperature and of Na/PO_4 molar ratio (over the range 1.0 to 3.0). Electrochemical testing is being initiated to measure corrosion currents with various temperature and chemical concentration gradients.

Plant Operations

Several near-term activities are planned which are related to plant operations:

- Eddy current examination of operating steam generators will be conducted when possible during refueling outages with emphasis on review of the data to detect any wall-thinning indications.
- Operating plants are being urged to remove sample inlet and outlet ends of steam generator tubes during refueling operations to allow detailed laboratory examinations of these tube sections.
- In light of laboratory developments in definition of the physical chemistry characteristics of sodium phosphate solutions, a lower limit of 2.3 on Na/PO_4 molar ratio is recommended. Eddy current examinations and PO_4 consumption/hideout tests are recommended prior to the implementation of the modified chemistry program.

LONG RANGE PROGRAMS

Alternate Tube Materials

Testing of alternate steam generator tube materials has been a continuing Westinghouse effort. Corrosion testing programs of steam generator tube materials were discussed in Section 4 of the Steam Generator Symposium document. Additional long range corrosion tests of these and other materials are continuing under various chemical environments which could be expected to occur in an operating steam generator under normal and abnormal conditions. These tests continue to show that Inconel-600 is superior to other candidate tube materials with respect to corrosion resistance over the range of expected chemical environments.

Wet Layup Chemistry

A program to evaluate Inconel-600 corrosion in typical wet layup chemical environments was begun in July, 1972, and is nearing completion. This program has indicated that no corrosion of Inconel-600 should occur in the specified wet layup chemical environment.

Chemical Cleaning

A program was initiated in January, 1973 to evaluate steam generator chemical cleaning agents for use if such cleaning is required. This program should be completed in late 1974. The following candidate cleaning processes have been selected for further evaluation.

a. Alkaline cleaning processes:
- Inhibited, sodium form, and ammoniated EDTA
- Ammonium persulfate ammoniated EDTA two-step process

b. Inhibited Acid Cleaning Processes:
- Inhibited ammoniated citric acid
- Inhibited sulfuric acid
- Inhibited hydroxyacetic acid

c. Acid-Alkaline Cleaning Process
- Inhibited sulfuric acid-ammonium EDTA Two-Step Process

Comparative evaluation of sodium-EDTA and ammonium-EDTA indicates that ammonium-EDTA is more effective in magnetite and sludge solution, especially if copper is present. On the other hand, ammonium-EDTA appears to be slightly more corrosive toward steam generator materials. However, the corrosivity of both sodium- and ammonium-EDTA toward Inconel-600 may be considered to be negligible, and this corrosion is reduced even further when the Inconel is mechanically coupled with carbon steel. Evaluation of these two chemicals as well as the other candidate cleaning agents is continuing.

Model Boiler Programs

Westinghouse has in progress several boiler test programs to further define the various thermo-hydrodynamic phenomena and to determine in more detail the magnitude and effects of chemical concentration and deposition which may occur in an operating steam generator. Some of these tests are described below.

- Crevice Model

  Experiments have been conducted to study the hydrodynamic character of boiling and the concentration of non-volatile solutes in annular tube crevices. These tests utilized electrically heated tubes to simulate the conditions at the tube-tube sheet joint in a steam generator. These studies showed that concentration can occur through boiling in tube crevices, and that this concentrating effect increases with increasing crevice depth and decreasing crevice width. The results of these tests support the change to construction of steam generators with tubes rolled the full depth of the tubesheet.

- Flow Visualization Model
  Westinghouse is sponsoring tests at a major university to obtain information on flow patterns in the lower part of the tube bundle and to provide further experimental data to verify thermal-hydraulic computer codes used in design analysis of Westinghouse steam generators. The model which was developed for these tests is shown in Figure 3-1. The test assembly consists of a two dimensional electrically heated Inconel tube bundle simulating the hot and cold legs of a steam generator with flow directing plates to simulate the tube wrapper. Refrigerant-113 is employed as the boiling, two phase heat transfer medium, and flow patterns can be photographed through viewports.

- Single Tube Test Boilers
  Several single-tube model boilers of the type shown in Figure 3-2 are being installed in a reactor coolant test loop at the Westinghouse Forest Hills site and at the Westinghouse R&D labs. These 3-kilowatt boilers simulate actual primary and secondary temperature, pressure and chemistry conditions, and all significant thermal and hydraulic parameters can be monitored. The objective of this test program is to determine the nature of chemical concentration and/or deposition

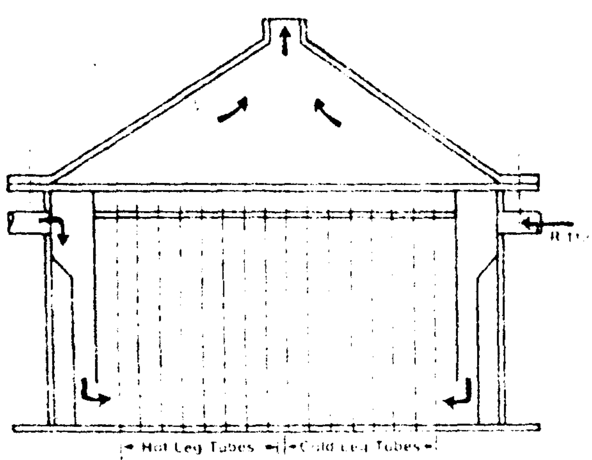


Figure 3-1
Flow Visualization Model

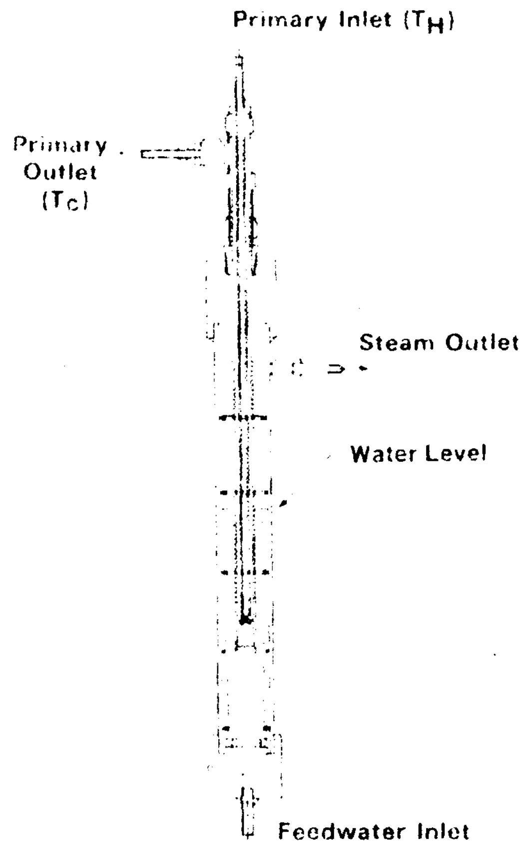


Figure 3-2
Single Tube Test Boiler

at the secondary surface of the tube, and to determine the corrosivity of chemical solutions toward Inconel-600 under steam generator heat transfer conditions.

- Other Model Boilers
  Further boiler tests are planned which will more closely simulate the actual conditions in an operating steam generator. Conceptual design has been completed for a 10 MW, 64 tube boiler, and construction will begin in 1974.

Special In-Service Examinations

- In-Bundle Boroscope Examinations
  A program of inspection of the secondary side of the steam generator tube bundle near the tube sheet has been initiated. This program consists of visual examination of the central part of the bundle by using a fiber-optics boroscope, to determine the amount of sludge deposited on the tube sheet. Results of the examination of a typical operational steam generator are shown in Figure 3-3. Further examinations of operating steam generators are planned to characterize the deposits formed and to determine any relationship between the nature and extent of deposits and tube performance.

- In-Bundle Probe
  A sampling probe has been developed and installed in one steam generator of Point Beach I and in one steam generator at Prairie Island. This probe is pictured in Figure 3-4. The in-bundle probe program will study the behavior of the steam generator bulk liquid within the tube bundle near the tube sheet at various plant operating conditions. The probe is designed to take temperature measurements and liquid

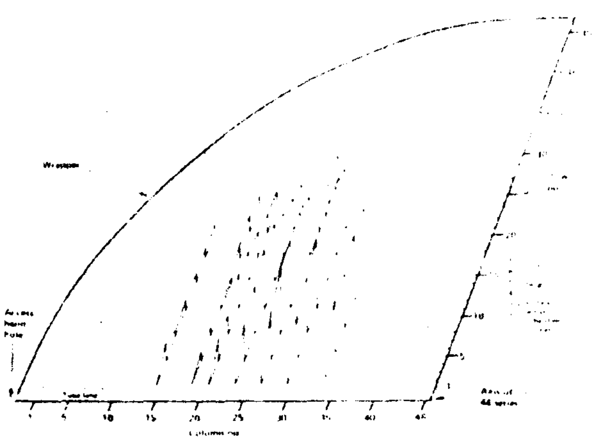


Figure 3-3
Surface of Crud Located by Fiber Optics Borescope Plus Depth Gage, Above the Cold-Leg Side of Tube Sheet of an Operational Steam Generator

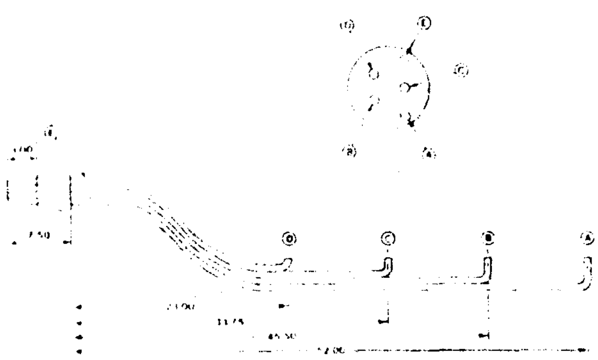


Figure 3-4
In-Bundle Probe

samples at four points in the hot leg of the tube bundle near the tube sheet. The location of the probe within the bundle is shown in Figure 3-5.

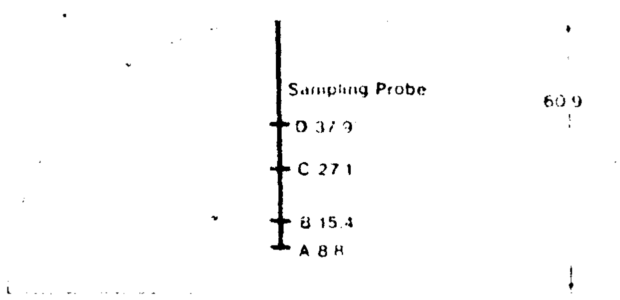


Figure 3-5
Location of In-Bundle Probe

The samples and thermocouple readings taken at various points within the bundle can be analyzed to determine any temperature and chemical concentration gradients which may develop in the steam generator during power operation. Typical temperature profile data is shown in Table 3-1. This temperature profile indicates the absence of superheat conditions near the tubesheet.

TABLE 3-1
TEMPERATURE PROFILE DATA TAKEN WITH IN-BUNDLE PROBE

96.97% Power

T_{SAT} = 517°F

TCA	Tubelane	507°F
TCB	Center	517°F
TCC	Center	512°F
TCD	Center	512°F
TCE	Down Comer	490°F

Chemical measurements thus far show no chemical gradient across the face of the tubesheet. Chemical concentrations of all in-bundle samples range between 6 and 8 per cent lower than blowdown concentrations, which is not believed to be significant.