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CORROSION OF STEAM GENERATOR TUBING IN OPERATING PRESSURIZED WATER REACTORS

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ABSTRACT

Corrosion of steam generator tubing has been observed in all but three PWR's that have been in operation for more than one year. The history of this experience with both stainless steel and Inconel-600 tubing is reviewed. Both intergranular stress corrosion cracking and localized, transgranular wastage have been observed with Inconel-600 tubing. The wastage can be attributed to a localized concentration, or "hideout" of phosphates in limited flow areas. A model is proposed for this wastage phenomenon which is consistent with operating experience.

INTRODUCTION

Corrosion of steam generator tubing has been observed in all but three of the fifteen pressurized water reactors (PWR's) in the U. S. that have been in commercial operation for more than one year as of June, 1974, as well as in five similar plants in other countries (1, 2, 3, 4, 5). The extent of damage has ranged from shallow attack on a few isolated tubes in some plants to complete penetration of several tubes accompanied by measurable attack on nearly half the tubes in one plant. Thus corrosion of steam generator tubing has become a generic problem of a magnitude that was totally unexpected with Inconel-600 tubing. In this paper, this operating experience will be summarized and a possible mechanism proposed for the observed wastage phenomena that is consistent with this experience.

Figure 1 is a schematic drawing of a typical PWR, taken from the Westinghouse Steam Generator Symposium (1). In the steam generators, the heat from the primary coolant is used to produce steam, which in turn passes through the turbine-generators to the condensers, where the waste heat is removed. Typical dimensions and operating parameters for the current design of nuclear steam generators are given in Table 1, taken from the Standard Safety Analyses Reports submitted by Westinghouse (6) and Combustion Engineering (7) and The Babcock and Wilcox Company (8).

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Figures 2 and 3 are cutaway drawings of U-tube steam generators of the type manufactured by Westinghouse (9) and Combustion Engineering, (10) respectively. To restrain the tubes from vibration, a series of supports are required for the straight portions of the tubes, and a series of restraints either in the form of anitivibration bars (Figure 2) or "bat-wings" (Figure 3) are used for the curved portions of the tubes. These supports frequently serve the additional function of baffling the flow of the secondary coolant to produce a lateral as well as vertical component to the flow. Figures 4 from (1) and 5 from (11) are photographs of steam generator tubing bundles in the assembly stage, and show the relation between the tubes and tubing supports.

STEAM GENERATOR WATER TREATMENT

Impurities carried into the steam generator by the feedwater tend to concentrate there, and precipitate as boiler scale on the high heat flux surfaces. The main sources of these impurities are corrosion of materials in the turbine, condenser, and feedwater piping, and inleakage of the tertiary coolant into the condensate. Two approaches to steam generator water treatment have been followed to control the formation of this cale: a "volatile" treatment in which the pH of the deionized water in the steam generator is raised and the oxygen scavangered by volatile additives such as hydrazine or morpholine, and a coordinated phosphate treatment in which sodium phosphates are added to the coolant to raise the pH and react with scale-forming impurities to produce relatively harmless soft phosphate precipitates, coupled with additions of hydrazine, morpholine, or sodium sulfite to scavange the oxygen. Both approaches have been used successfully in some instances; both have led to difficulties in some instances.

THE "VOLATILE" TREATMENT OF STEAM GENERATOR COOLANT

In a U-tube steam generator of the types shown in Figures 2 and 3, recirculation ratios of boiler waters generally range from 2/1 to greater than 5/1. Therefore it is not deemed necessary to maintain extremely pure water in the steam generators at all times. Hydrazine and/or morpholine are added to the feedwater as required to maintain a pH in the rage 8 to 9. The coolant is continuously monitored for pH and conductivity, and periodically sampled and analyzed for dissolved and suspended solids. High conductivity and impurity levels in the coolant are removed by blowdown and additions of deionized makeup water. Typical normal operating limits are given in Table 2, taken from (12). Condenser inleakage of impurities is indicated by condensate conductivity monitors. Continuous demineralization of all or part of the condensate is being considered for some plants (13, 14).

For plants with "once-through" steam generators, full-flow condensate demineralization and extremely stringent control of feed-water purity are required to prevent scale formation on the tubes. Typical operating limits for impurity levels in once-through boilers are also given in Table 2, taken from (8) and (13).

THE COORDINATED PHOSPHATE TREATMENT OF STEAM GENERATOR COOLANT

This method has been used in most PWR's. In principle, demineralized water is used for the secondary coolant to which disodium orthophosphate (Na_2HPO_4) is added to form insoluble, but soft precipitates of metal (i.e., Fe or Ca) phosphates which can, in principle, be removed by blowdown (1, 9). The reaction sequence that occurs can be described as follows for Ca ions entering the solution through condenser inleakage as $Ca(HCO_3)_2$:

$$6\ Na_2HPO_4 + 3\ Ca(HCO_3)_2 \rightarrow Ca_3(PO_4)_2 + 4\ Na_3PO_4 + 6\ CO_2 + 6\ H_2O \quad [1]$$

but trisodium phosphate tends to hydrolyze in solution by the reaction

$$Na_3PO_4 + H_2O \rightarrow Na_2HPO_4 + NaOH \quad [2]$$

so that the end products become calcium phosphate and sodium hydroxide; consequently, without proper controls, conditions that promote caustic stress corrosion cracking can develop.

Reaction [2] tends to proceed to the right as written unless the average mol ratio of Na/PO_4 in solution is equal to or less than 2.6/1 to 2.8/1, depending on the temperature, the nature of other ions in solution, etc.; pH changes also occur during these reactions. The general relation between pH, concentration of phosphate ions, and tendency to form free caustic is given in Figure 6, taken from the work of Marcy and Halstead (15) as adopted by Westinghouse (1, 9).

The pH of the secondary water will be raised by reactions similar to [1] and [2] only if the metal ions that precipitate as phosphates enter the condensate in the form of hydroxides (i.e., $FeO{\cdot}H_2O$ or $Fe(OH)_2$ from corrosion products) or carbonates or bicarbonates. Metal chlorides or sulfates entering the condenser (i.e., $CaCl_2$ or $MgSO_4$) will tend to lower the pH of the secondary coolant by reactions of the type,

$$3\ MgSO_4 + 2\ Na_2HPO_4 \rightarrow Mg_3(PO_4)_2 + 2\ Na_2SO_4 + H_2SO_4 \quad [3]$$

Inleakage of traces of NaCl should not have an effect on the solution pH, since no insoluble phosphates are formed.

Condenser leakage at inland locations where hard waters are common will, in general, tend to raise the solution pH and may promote caustic attack. Condenser leakage at coastal plants will, in general, tend to lower the solution pH (due to $MgCl_2$ intrusion) and may promote acid attack. Consequently, any secondary water monitoring program must be designed with the composition of the condenser coolant in mind to give adequate warning of condenser leakage.

In the application of the coordinated phosphate treatment, phosphates are normally added continuously to the secondary coolant as disodium phosphate, or a mixture of di-and trisodium phosphates. The phosphate sludge is removed, along with other impurities in the steam generator coolant, by continuous blowdown (1, 9). Typical operating limits and sampling controls are shown in Table 3, taken from (9).

CORROSION PHENOMENA

The concentrations of impurities found in steam generator coolants would normally be harmless to the materials of construction, primarily Inconel-600 and carbon or low alloy steel. However, the heat flux through the steam generator tubes provides a concentrating mechanism for impurities. The surface of the steam generator tubing is generally 25-50°F hotter than the surrounding coolant. Ideally, as steam bubbles form at the surface, there is sufficient turbulence in the coolant to sweep them away and prevent increases in concentration and/or precipitation of impurities on the tubing surface. However, the need for mechanical restraint of the tubes to dampen vibration, and the tendency for sludge to accumulate on the surface of the tube sheet and/or tube supports can give rise to local sites where the coolant is boiled away more rapidly than it is replaced, and therefore, locally high concentrations of impurities.

Figure 7 shows a schematic representation of the concentrating processes in the area of sludge deposition on the tube sheet surface, taken from (1). Similar concentrating mechanisms are applicable in the vicinity of tubing supports of the type sketched in Figure 8, and in tube to tube sheet crevices, of the types shown in Figure 9, taken from Weber and Sury (16). Concentration factors of $>10^4$ have been postulated to occur in these areas, so that a few ppm of NaOH produced by a reaction sequence of the type given above, or by inleakage of impurities (such as Na_2CO_3 or KNO_3) that tend to decompose to form caustic in the steam generator (17), can build up locally to several weight percent and give rise to stress corrosion cracking of the Inconel tubing, especially in the hot leg side of the U-tube steam generator, where the temperature differential between the primary and secondary coolants is the greatest. Phosphates also tend to be concentrated (hideout) in these areas, and then to reappear in solution whenever a power reduction and its concomitant reduction in heat flux allows the coolant to flush out these areas (inverse hideout). The experience with inverse hideout in one plant is described in Table 4, taken from (18). These hideout phenomena have led to stress corrosion cracking or a general wastage attack in operating plants.

STRESS CORROSION CRACKING

Stress corrosion cracking of the Inconel-600 tubing by hideout of NaOH in the tube to tube sheet crevices or in the area of sludge buildup on the tube sheet has produced leaks in several plants (1, 2, 3, 4, 5, 16). Careful control of the phosphate additions in the manner described above and in Table 3 has been demonstrated to eliminate this attack (1), as described below under plant operating experience. Intergranular stress corrosion cracking of Inconel by pure water in crevice areas has been reported in laboratory tests, but has not been observed to date in operating steam generators. Figure 10 shows a micrograph of the intergranular stress corrosion that occurred just above the tube sheet in one plant.

WASTAGE OR PITTING ATTACK

A generalized transgranular corrosion or wastage of Inconel-600 has been observed in the vicinity of tubing supports of the type shown in Figure 8, or in the area of sludge accumulation above the tube sheet.

This attack has only been observed with the coordinated phosphate treatment of steam generator coolants, and is believed to be caused by a reaction between nickel and sodium hydrogen phosphates. A mechanism for this attack is proposed in the discussion section below. Figure 11 shows the nature of the attack in the vicinity of tubing supports in one plant (14).

A similar phenomenon has been observed in one plant after an extended period of "dry layup," during which the coolant had been drained, and the steam generators filled with air, without the sludge deposits having been dried (18). In this case the pits were observed both in areas in which wastage had occurred during operation of the plant, and in new areas, unrelated to "normal" areas of sludge deposition, in the upper half of the steam generator tubing. This attack is shown in Figure 12. A local intergranular attack was found in the same general area, a micrograph of which is also shown in Figure 12.

CORROSION EXPERIENCE IN OPERATING PWR's

The author has prepared a detailed review of the corrosion experience in each operating PWR.

This experience is summarized below.

PLANTS WITH STAINLESS STEEL STEAM GENERATORS

Five of the early commercial nuclear power stations were built with stainless steel steam generators. These include Shippingport, Yankee - Rowe, Indian Point-1, and the Hanford "N"-reactor, which are PWR's, and Peach Bottom-1, a gas-cooled reactor. Sensitization of the stainless steel tubing during heat treatment of the carbon steel tube sheets led to stress corrosion cracking and leakage in the "N"-reactor and in Peach Bottom-1 during the preoperational hydraulic pressure tests (4). The steam generators of both plants were retubed prior to startup, the "N"-reactor with Inconel-600, and Peach Bottom-1 with Incoloy-800. Leaks due to stress corrosion cracking developed at Shippingport within 200 hours of power operation in December, 1957 (4). A high phosphate treatment was then adopted (100-300 ppm added as Na_2HPO_4) (19) and the plant operated until 1964, when the steam generators were replaced with larger units tubed with Inconel-600 (20).

Indian Point-1 (21, 22) and Yankee - Rowe (23) have had a series of shutdowns for steam generator leaks. Both plants use a zero solids water treatment to minimize the probability of stress corrosion cracking (22, 24). Neither uses condensate demineralization. Most of the problems at Indian Point-1 have been in one area of one (horizontal) steam generator, where the tubing supports have sagged, creating a locally high stress on the tubes (22).

PLANT WITH INCOLOY-800 STEAM GENERATORS

Since the steam generators at Peach Bottom-1 were retubed (in 1967) with Incoloy-800, no corrosion problems have developed (25). Inservice eddy current inspections have revealed no defects. A zero solids treatment of the secondary coolant is used, with full-flow demineralization of the condensate. During layup periods the steam generators are blanketed with nitrogen.

PLANTS WITH INCONEL-600 STEAM GENERATORS

Plants Using a Zero Solids Treatment:

Four plants have operated for more than one year with a zero solids treatment of their secondary coolant. No steam generator corrosion or leakage has occurred at Maine Yankee (14) and Oconee-1 (26). The wastage attack observed at Shippingport when phosphate chemistry was used was essentially eliminated by the adoption of a zero solids water treatment in 1971 (20). Stress corrosion cracking of the steam generator tubing occurred in the crevice between the tubes and tube sheet at Beznau-I during the initial zero solids operation (1, 16). Condenser inleakage occurred during this period, which is believed to have introduced impurities (such as nitrates or carbonates of sodium or potassium) that partially decomposed in the steam generators to form hydroxides of sodium or potassium, which in turn led to stress corrosion cracking of the tubing. The possibility that attack could have been a manifestation of the stress corrosion of Inconel tubing by "pure water" in crevice areas cannot be discounted at this time.

The 10 of the 12 steam generators in the "N"-reactor that were retubed with Inconel-600 prior to startup have operated in a trouble-free manner since April, 1966, with no measurable leaks detected during pressurization, other than a slight weepage of F^{18} (27). (Leaks in the two remaining stainless steel steam generators have caused an average of two tubes per year to be plugged.) Feedwater is limited to 150ppb Cl^-. Full-flow condensate demineralization is available for startup or shutdown conditions, or whenever condenser leakage occurs. The tubes were expanded the full depth of the tube sheet by rolling, as in Figure 9C.

<u>Plants Using a Coordinated Phosphate Treatment:</u>

Seven plants that started operation in the period 1967-71 used originally a low (5-10 ppm) phosphate treatment of the secondary coolant. Because of condenser inleakage, it has been found difficult to maintain phosphates in this range without free caustic developing from reactions such as [1] and [2]. Consequently, stress corrosion cracking of the tubing in the area of sludge buildup on the tube sheet surface has occurred in several of these plants, including Connecticut-Yankee, Point Beach-I, H. B. Robinson-II, Zorita (in Spain), and in Beznau-I after the water chemistry was switched to a low phosphate treatment in September, 1971 (1). At the same time that stress corrosion was developing in the above cited plants, steam generator leaks due to wastage developed in the vicinity of tubing supports in Mihama-1 (1), Palisades (28) and Shippingport (20). Of these, Mihama-1 and Palisades were operating on a low-phosphate chemistry (14), and Shippingport on a high (100-300ppm) phosphate chemistry (19). Only the R. E. Ginna and San Onofre plants operated without steam generator corrosion when using a low phosphate treatment.

In mid-1972, the low phosphate treatment was abandoned at all the above-cited plants (except Shippingport, which switched to zero solids in 1971) in favor of a higher coordinated phosphate treatment of the type described above, and in Figure 6, coupled with, in most cases, continuous blowdown in an attempt to minimize sludge buildup (1, 9). This change appears to have eliminated the stress corrosion cracking phenomenon; in the Robinson-II plant, a 75% through wall stress corrosion crack observed originally in 1972 was reinspected one year later and found to be unchanged following the increase in phosphate concentration (29).

However, increasing the phosphate concentration appears to have increased the probability of wastage developing in the area of tubing supports at Palisades and Mihama-1 (14), and in the area of sludge buildup on the tube sheet in R. E. Ginna (30), San Onofre 1 (1) and Zorita (1) of the older plants, and in Beznau-II (1) and Surry-I (17) both of which started up with the higher phosphate treatment. Measurable wastage has been observed on nearly half the 8000+ tubes in each steam generator at Palisades (31), and on approximately 15% of the tubes of the tubes in one of the Ginna steam generators (30). Further, significant additional wastage occurred at Palisades during the "dry" layup repair period, both in the areas of tubing supports and in "new" areas between supports in the upper part of the steam generator (18). This phenomenon is shown on Figure 12. This plant will switch to an all-volatile treatment, of the type shown in Table 2, upon the next startup.

DISCUSSION

The corrosion experience in the steam generators of operating nuclear plants, as summarized above, has led to a dilemma for the plant operator: should he risk stress corrosion cracking in crevice areas (as in Beznau-I) by adopting a zero solids treatment, or risk stress corrosion cracking or wastage by adopting a phosphate treatment, paying strict attention to sodium/phosphate ratios and to hideout-inverse hideout phenomena (which are indicators of a wastage attack)? The evidence cited above suggest that a zero solids treatment coupled with condensate demineralization offers the fewest potential sources of difficulties, but there is too little long-term experience with such a treatment and Inconel-600 tubes, especially in plants with tube to tube sheet crevices of the type shown in Figure 9 A and B, to provide any assurance that this approach will be comparatively trouble-free. The liklihood that integranular stress corrosion of the Inconel by "pure" water (the Coriou effect) may develop in crevices in these systems cannot be discounted at this time. Further, there is too little understanding of the causes of wastage at this time to permit design of a phosphate treatment to minimize wastage attack.

MECHANISMS OF WASTAGE

In another paper at this symposium, Panson et al (32) have given solubility and phase relation bases for an improved phosphate control, based on the assumption that it is precipitation of sodium phosphates with a Na/PO_4 mol ratio <2.1 that lead to the wastage attack. These experiments have also been described in (1), second supplement. The hideout and inverse hideout data given in Table 4 suggest that Na/PO_4 in these precipitates may vary from 1.9 to 2.8.

We suggest the following alternate mechanism for the wastage attack, which does not require that "hideout" phosphate deposits have a low Na/PO_4 ratio. The data from Palisades, given above in Table 4, suggest that during inverse hideout in this plant, Na/PO_4 ratio changed in either direction i.e., from 2.4 to 2.8, or from 2.6 to 2.0 - on several occasions.

In the hideout areas where the phosphate-rich sludge forms, we suggest that the nickel is replacing the hydrogen ions in the sodium hydrogen phosphates by a reaction of the general type:

$$2\ (Na_2HPO_4) + Ni \rightarrow Na_4\ Ni\ (PO_4)_2 + H_2 \qquad [4]$$

Cowan and Staehle (33) have studied the thermodynamics and electrode kinetic behavior of nickel in high temperature solutions. An Emf-pH (Pourbaix) diagram for the nickel-water system at 300°C from their paper is shown in Figure 13. The nickel oxides that are quite protective at 25°C are seen to become unstable with respect to the $HNiO_2^-$ ion at a pH at 300°C >9. Further, their calculated electrochemical potentials suggest that oxidation of Ni by water to form $HNiO_2^-$ (or NiO) and H_2 will just about balance at 1 atm H_2; at lower pressures of H_2 these oxidation processes will occur, and continue, especially when the non-protective $HNiO_2^-$ species is formed.

The room temperature pH of solutions of sodium phosphates has been estimated by Westinghouse (14) as a function of the Na/PO_4 ratio and phosphate concentrations. These results are shown in Figure 14. At 1000 ppm PO_4 the calculated room temperature pH is seen to be $\geq$11 at all Na/PO_4 ratios $\geq$2. Therefore, in phosphate hideout areas, the non-protective $HNiO_2^-$ ion rather than the protective NiO is the stable phase. We suggest that the wastage is due to a reaction such as [4], promoted by the absence of a protective oxide on the nickel, and that the greenish corrosion products observed adjacent to wastage areas contains some mixture of sodium nickelites and sodium nickel phosphates.

Reactions of the protective NiO with water to form $HNiO_2^-$ when Na_3PO_4 is present may be responsible for intergranular stress corrosion when "free caustic" is present (as suggested by Cowan and Staehle); but the absence of wastage attack in those plants in which stress corrosion was observed suggests the precipitation of sodium hydrogen phosphates is necessary for wastage to occur. Formation of $HNiO_2^-$ in the hideout areas may also serve to depassivate the Inconel, so that more noble metals, such as copper ions from condenser corrosion, may precipitate on the Inconel surface in these areas, and give rise to local galvanic cells that can become active when the steam generator is exposed to air during layup periods, and cause pitting of the type observed at Palisades, shown in Figure 12.

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REFERENCES

1. The Westinghouse Steam Generator Symposium, Westinghouse Nuclear Energy Systems, April, 1973, including Supplement #1, July, 1973, and Supplement #2, December, 1973.

2. P. D. Stevens-Guille, "Steam Generator Tube Failures: A World Survey of Water-Cooled Nuclear Power Reactors to the End of 1971" AECL-4449, April, 1973; also "World Experience in Water-Cooled Nuclear Power Reactors During 1972," AECL-4753, March, 1974.

3. J. R. Weeks, "Corrosion of Steam Generator Tubing in Operating Pressurized Water Reactors" Materials Engineering Branch, Directorate of Licensing, June 22, 1973; also Revised Edition July 1, 1974.

4. S. H. Bush and R. L. Dillon (PNL), "Stress Corrosion in Nuclear Systems," Paper Presented at International Conference on Stress Corrosion Cracking and Hydrogen Embrittlement of Iron-base Alloys, Firminy, France, June 12-16, 1973.

5. M. A. Cordovi, Corrosion Considerations in Light Water Cooled Nuclear Power Plants, Paper No. 7, International Nickel Power Conference, Kyoto, Japan (1972).

6. W RESAR-41 (Westinghouse Reference Safety Analysis Report) December, 1973.

7. CESSAR (Combustion Engineering Standard Safety Analysis Report, System 80) (1974).

8. B-SAR-241 (Babcock and Wilcox Standard Safety Analysis Report) (2/21/74).

9. W. D. Fletcher and L. F. Picone, "Secondary Water Treatment of PWR Steam Generators," Paper presented at International Water Conference of the Engineers Society of Western Pennsylvania, Pittsburgh, October, 1972.

10. Final Safety Analysis Report, Palisades Reactor Docket #050-00255.

11. "Nuclear Power Systems," CE, Combustion Division.

12. Palisades Reactor, Docket #050-00255, Responses to AEC Questions, Letter, R. B. Sewell to R. J. Schemel March 20, 1974, including Attachment A.

13. F. J. Pocock, J. H. Hicks, N. J. Mravich, and M. J. Bell, "Water Chemistry for PWR Nuclear Steam Supply Systems" Babcock and Wilcox Technical Paper Presented to 10th Annual Liberty Bell Corrosion Course, Philadelphia, September, 1972.

14. P. E. C. Bryant and W. P. Chernock (Combustion Engineering) Private Communications, 6/29/73, 10/19/73, and 12/12/73.

15. V. M. Marcy and S. L. Halstead, Combustion, January (1964) 45-47.

16. J. Weber and P. Sury, "Intergranular Stress Corrosion Cracking of Nickel Alloys in Pressurized Water" Paper #54, Corrosion/74, Chicago, March, 1974, N.A.C.E., Houston.

17. W. D. Fletcher, Westinghouse Nuclear Energy Systems, Private Communications, 7/18/73, 12/5/73, and 2/14/74.

18. R. B. Sewell, L. Stretz, and D. M. Noble, Consumers Power Company, Private Communications, 6/12/74.

19. W. J. Singley, I. H. Welinsky, S. F. Whirl, and H. A. Klein, Proc. Am. Power Conf. 21 (1959) 748-68 (also published as WAPD-T-939).

20. Private Communication.

21. Consolidated Edison Company of New York, Inc., Indian Point 1 PWR, Semiannual Operations Report Nos. 4 (Feb.-July 1964), 5 (Aug. 1964-Jan. 1965), 6 (Feb.-July 1965), 8(Feb.-Sept. 1966), 9 (Oct. 1966-March 1967), 10 (April-Sept. 1967), 11 (Oct. 1967-March 1968), 12 (April-Sept. 1968), 13 (Oct. 1968-March 1969), 14 (April-Sept. 1969), 15 Oct. 1969-March 1970), 16 (April-Sept. 1970), 18 (April-Sept. 1971), 19 (Oct. 1971-March 1972), and 20 (April-Sept. 1972). Docket File 50-003.

22. H. H. Bahrenburg, A. W. Flynn, S. Rothstein, P. Skulte, and A. W. Zeuthen, "Materials Performance at the Indian Point Nuclear Station," Symposium on Materials Performance in Operation Nuclear Systems, Ames, Iowa, August, 1973, Pg. 229 M. S. Wechsler and W. H. Smith, Editors. CONF-730801.

23. Yankee Rowe, Docket #50-29, Monthly Operations Report Nos. 75 (March 1967), 79 (July 1967), 111 (March 1970), 116 (August 1970), 119 (Nov. 1970), 129 (Sept. 1971), and 131 (Nov. 1971).

24. C. Antonini, Yankee Atomic Electric Company, Private Communication, 6/13/74.

25. J. Cooney, Philadelphia Gas and Electric Company, Private Communication, 6/13/74.

26. M. J. Bell and D. F. Levstek, The Babcock and Wilcox Co., Power Generation Division, Private Communications, 8/22/73 and 6/11/74.

27. R. L. Dillon, Battelle Memorial Institute, Pacific Northwest Laboratories, Private Communications, 6/14/74 and 6/19/74.

28. Letters, R. B. Sewell (Consumers Power Co.) to J. F. O'Leary, 1/29/73 and 3/6/73, Palisades Docket File 050-00255.

29. Letter, E. E. Utley (Carolina Power and Light) to R. J. Schemel, 5/11/73, with enclosure, "Hydrostatic Testing of Steam Generators," H. B. Robinson, Unit No. 2, Docket File 050-00261.

30. Rochester Gas and Electric Corporation, "Description of Present Status of Steam Generators," 3/21/74, R. E. Ginna Docket File 050-00244.

31. Letters, R. B. Sewell (Consumers Power Co.) to J. F. O'Leary, 12/21/73 and 2/15/74, with enclosures.

32. A. J. Panson, G. Economy, C. Liu, T. S. Bulischeck, and W. T. Lindsay, Jr., "Sodium Phosphate Water Treatment for Nuclear Steam Generators, Solubility and Phase Relations Basis for Invariant Point Chemistry Control," this symposium.

33. R. L. Cowan and R. W. Staehle, J. Elect. Soc. 118 (1971) 557.

TABLE 1

CURRENT PWR STEAM GENERATOR DESIGN PARAMETERS

	Westinghouse (6)	Combustion Engineering (7)	Babcock & Wilcox (8)
Overall Height, ft	72	68	78
Overall Diameter, ft	a	22	a
Number of Tubes/Generator	4864	a	15,743
Length of Tubes, ft	b	b	56
MWt/generator*	954	1908	1909
MWt/tube*	0.20	a	0.13
Flow, 10^6 lb/h*	4.3	8.6	8.4
Max. Temperature, °F*	600	553	595

*At full load   a Not Given   b Variable (U-tubes)

TABLE 2

STEAM GENERATOR WATER CHEMISTRY SPECIFICATIONS, ZERO SOLIDS APPROACH

	Once-Through (8)	Recirculating (12)	
		Feedwater	Generator
pH	9.3-9.5	8.8-9.2	8.2-9.0
Cation conductivity (μmho/cm)	0.5	1	50
Oxygen (ppb)	7	10	--
Total solids (ppm)	0.005	--	50

TABLE 3

WESTINGHOUSE STEAM GENERATOR WATER CHEMISTRY SPECIFICATIONS FOR PHOSPHATE TREATMENT [FROM (9)]

pH (at 25°C)	8.5 - 10.6
Phosphate, ppm	10 - 80 (fresh water) 25 - 80 (brackish water)
Na/PO_4 molar ratio	2.0 - 2.6*
Free caustic	Zero
Total dissolved solids, ppm	125 maximum
Dissolved oxygen, ppb	Zero (<5)
Silica, ppm (maximum)	5
Chloride plus fluoride, ppm (maximum)	75

*Revised in 1974 to 2.3 - 2.6 (1).

TABLE 4

INVERSE HIDEOUT OF PHOSPHATES FOLLOWING POWER REDUCTIONS IN THE PALISADES REACTOR (18)

Date	ppm PO_4 in coolant		pH		Na/PO_4 mol ratio	
	before	after	before	after	before	after
12/72	41	150	--		2.4 A	2.05 A
			--		2.6 B	2.05 B
3/73	70	250	9.8	8.4	2.15 A	1.9 A
					2.3 B	2.1 B
4/73	110	1500	10	11.2	2.2	2.4
4/73	70	1000	10	11.5	2.4	2.8
6/73	25	1100	9.3	11	2.15	2.25
7/73	25	2100	--	10.9	2.3	2.2

A and B refer to A and B steam generator.

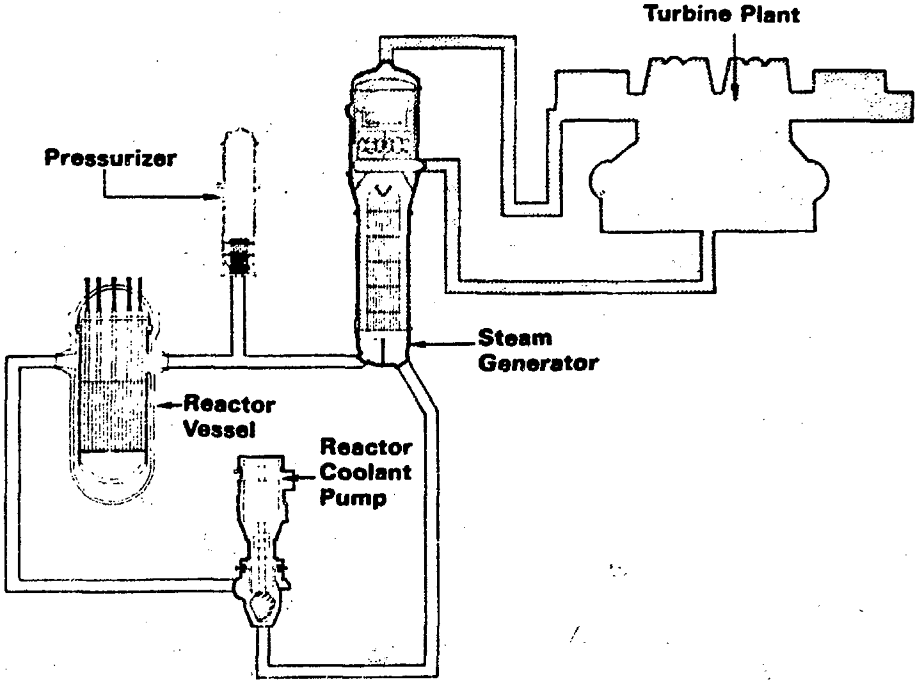


Figure 1 Schematic Representation of a PWR

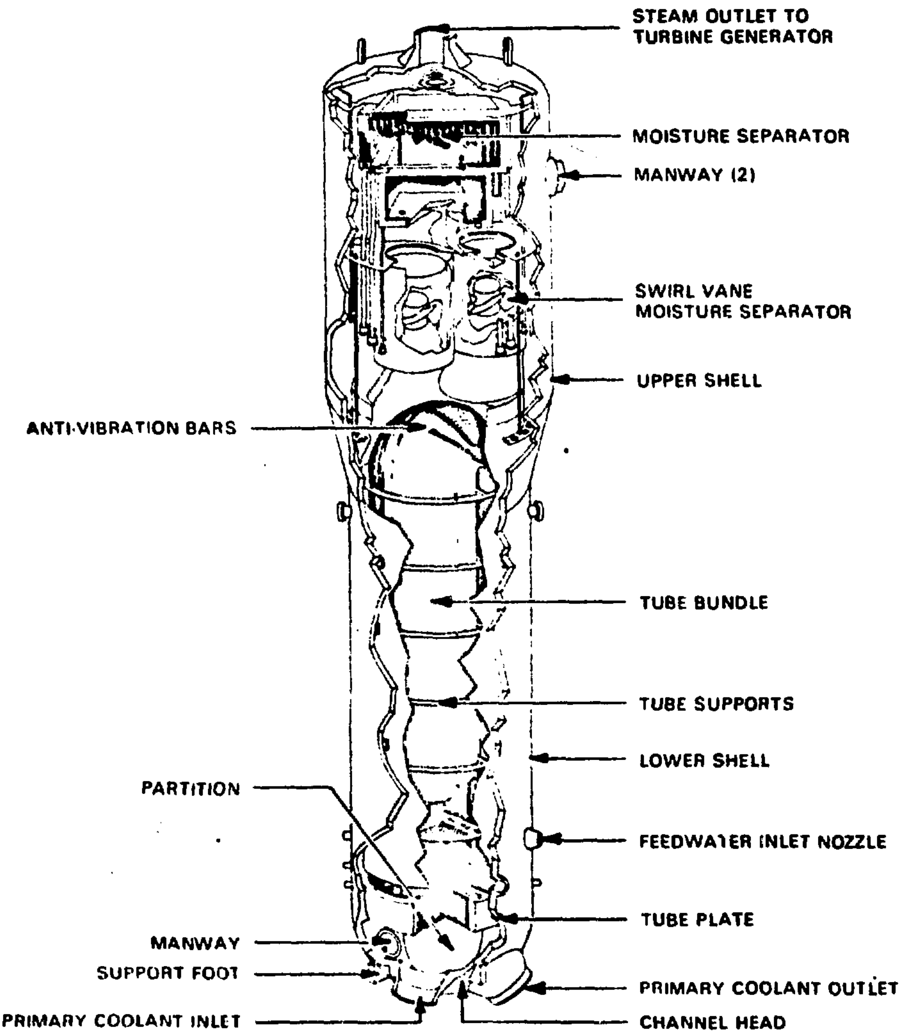


Figure 2 View of Typical Westinghouse Steam Generator

STEAM GENERATOR

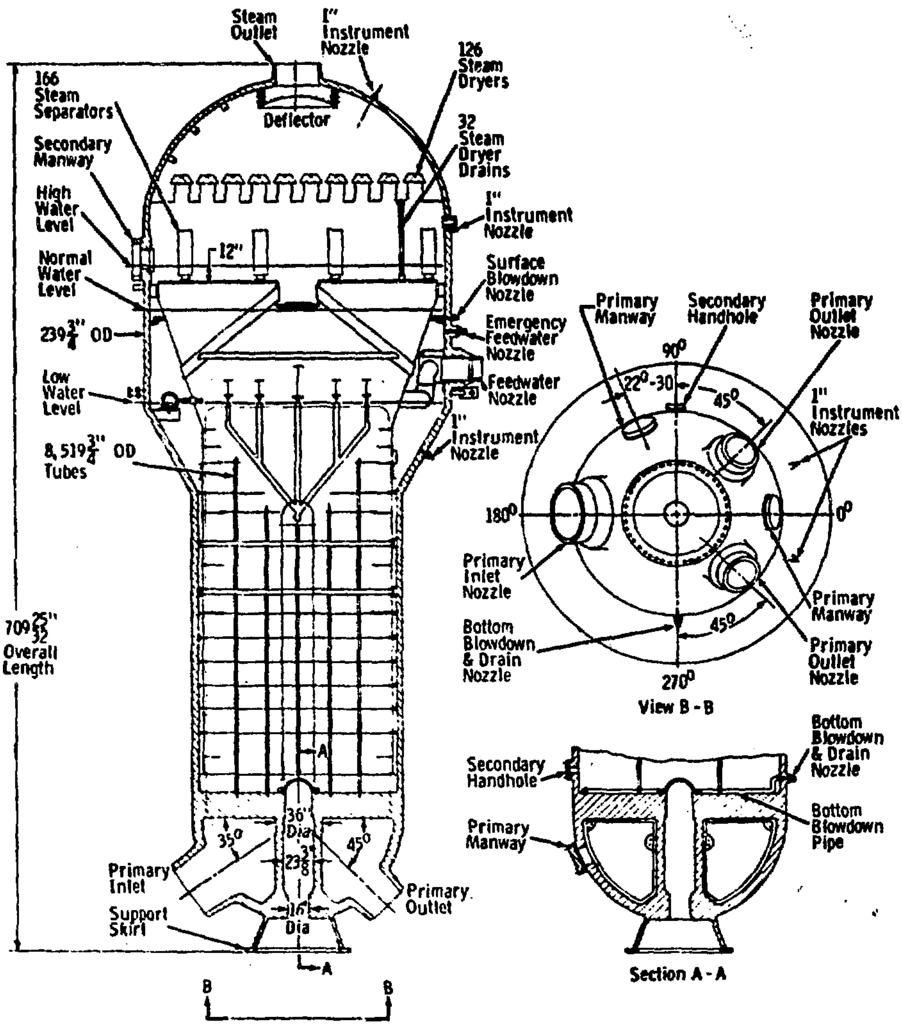


Figure 3 View of a Combustion Engineering Steam Generator

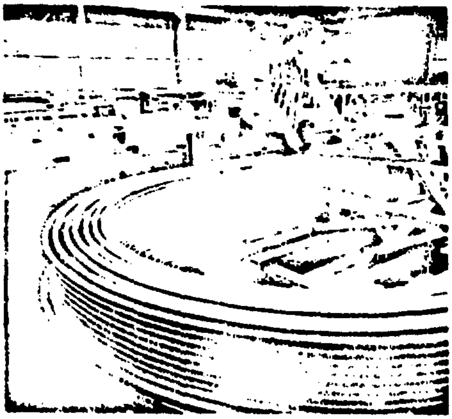


Figure 4 Assembly of a Westinghouse Steam Generator

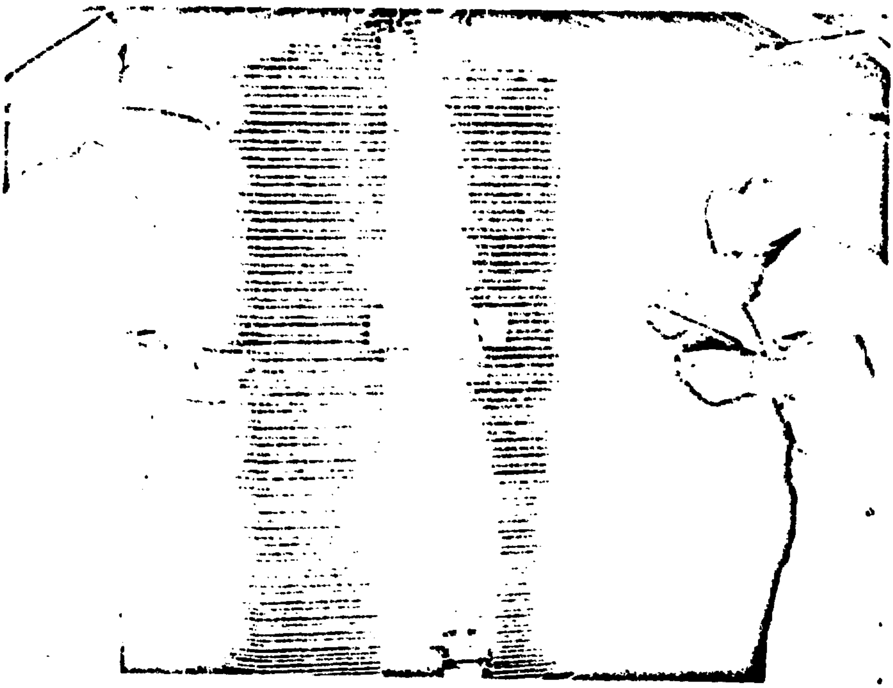


Figure 5 Assembly of a Combustion Engineering Steam Generator

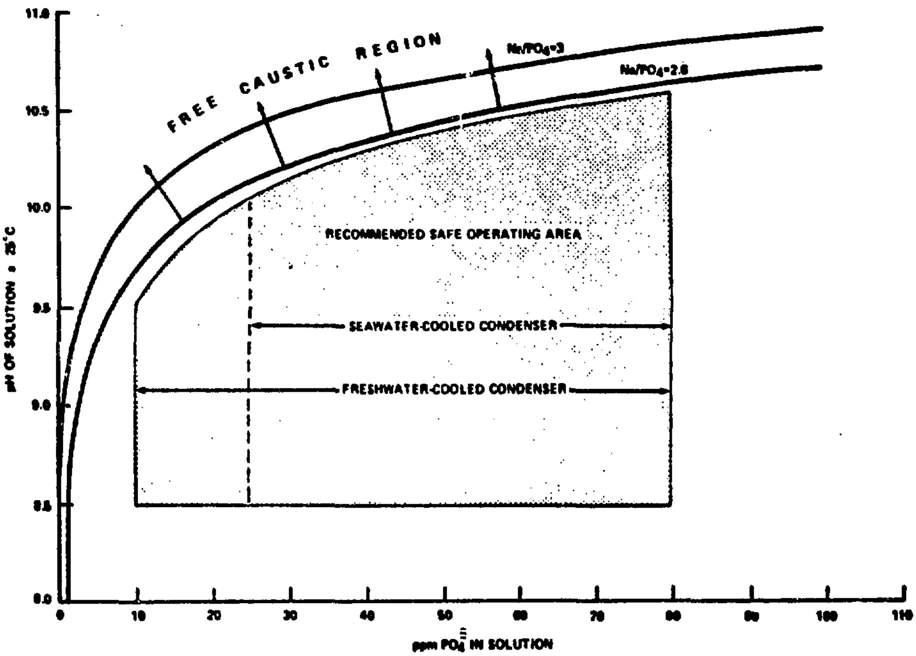


Figure 6 Relation Between pH and Phosphate Concentrations for Prevention of Stress Corrosion Cracking by Caustic

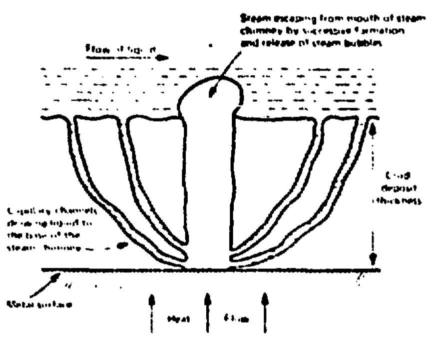


Figure 7 Schematic Representation of Concentration Processes in Sludge Deposits

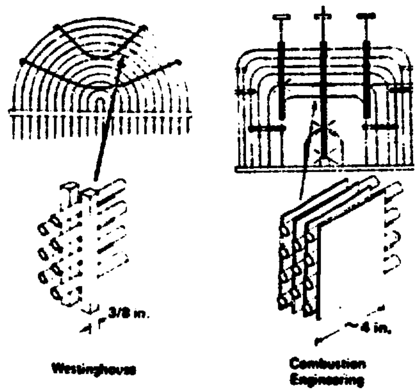
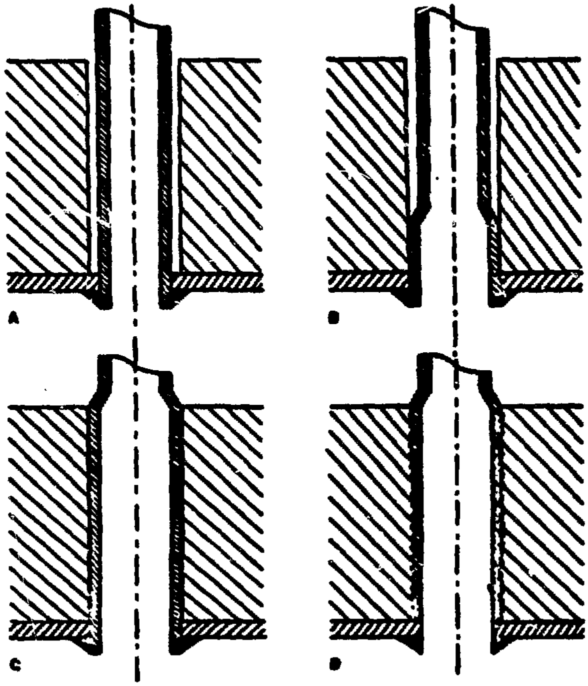
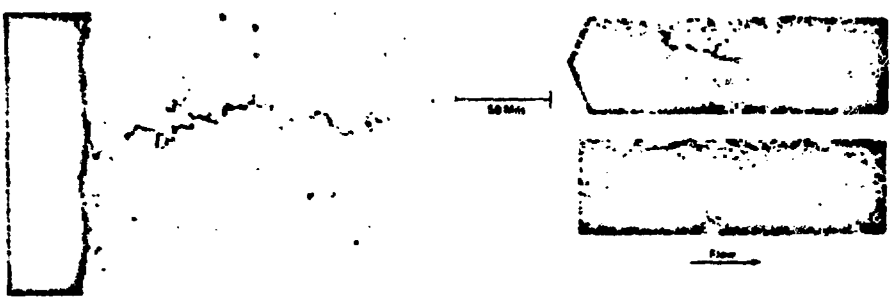


Figure 8 Schematic Representation of Tubing Supports in the Upper Portion of Steam Generators (1)



A welded
B partly rolled in and welded
C completely rolled in and welded
D explosion bonded and welded

Figure 9 Methods Used to Attach Tubes to Tube Sheets



100X
Micrograph of Intergranular Cracks

4 15/16" Above Tube Sheet

Figure 10 Stress Corrosion Cracking of Inconel-600 in the Area of Sludge Buildup on the Tube Sheet in the Robinson-2 Plant (1)

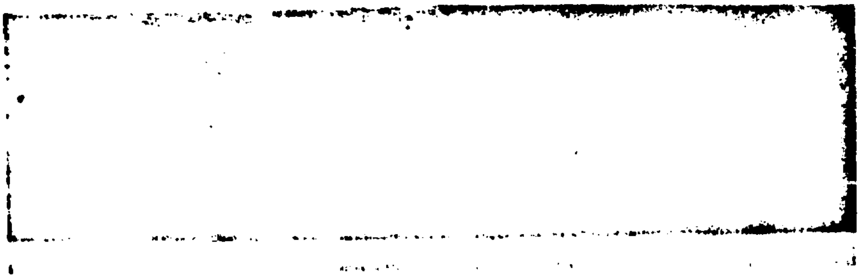


Figure 11 Nature of Wastage of Inconel in the Vicinity of Tubing Supports in the Palisades Reactor. The Defect Shown is 35 mils Deep. Flow was from Left to Right.

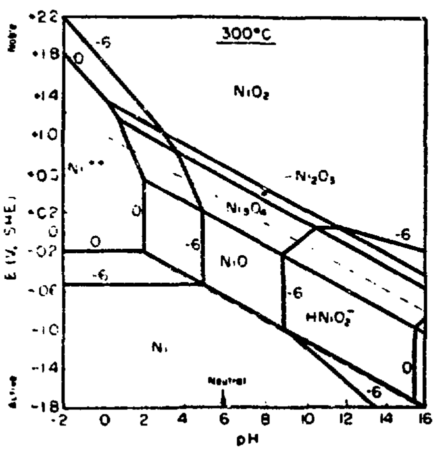
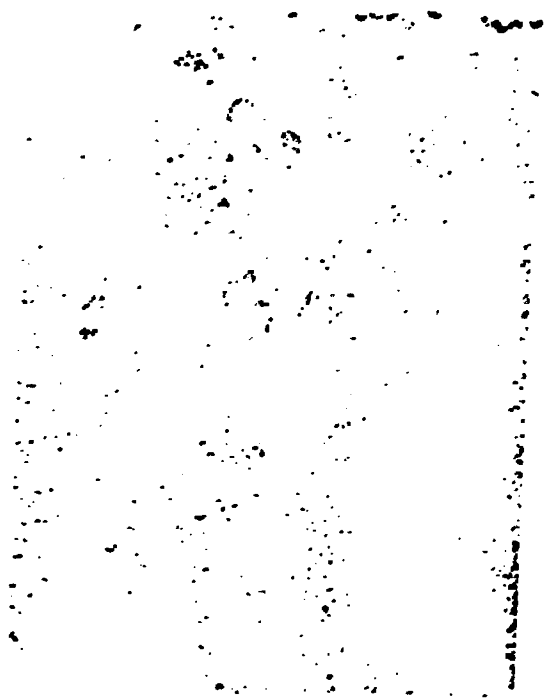


Figure 13 Potential-pH Diagram of Nickel-H_2O System at 300°C

Intergranular Corrosion that Developed at Palisades During Shutdown 125X



Corrosion Pit that Developed at Palisades During Shutdown

Figure 12 Micrographs from Battelle-Columbus Labs, Courtesy of Consumers Power Co.

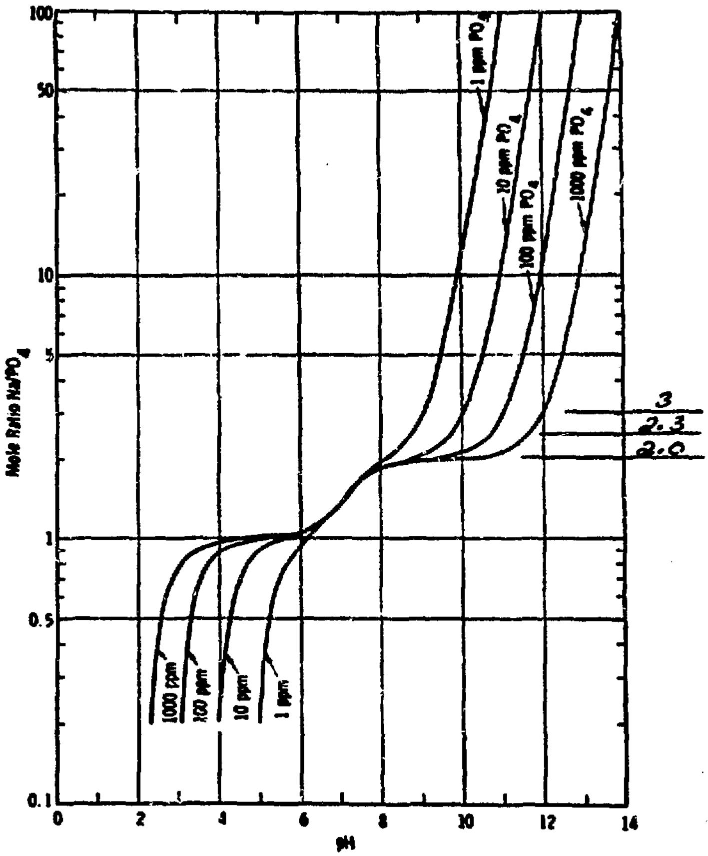


Figure 14 Estimated Relationship Between pH, Na/PO_4 Ratio, and Phosphate Concentration