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The Degradation of Steam-Generator Tubing and Components by Operation of Pressurized-Water Reactors*

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Experience in operating pressurized water reactors (PWR) has shown a number of materials degradation processes to have occurred in their steam generators. These include stress corrosion cracking (SCC), intergranular attack, generalized dissolution, and pitting attack on steam generator tubes; mechanical damage to steam generator tubes; extensive corrosion of tubing support plates (denting); and cracking of feedwater lines and steam generator vessels. The current status of our understanding of the causes of each of these phenomena is reviewed with emphasis on their possible significance to reactor safety and directions the nuclear industry and the NRC should be taking to reduce the rate of degradation of steam generator components.

INTRODUCTION

Operation of PWR steam generators has led to a number of degradation processes on the steam generator tubing, the support plates, the vessels, and the piping. These are listed in Table 1.

Table 1
Steam Generator Degradation Processes

A. <u>Tubing (Inconel-600)</u>
    Primary Side:
        SCC
        Intergranular Attack
    Secondary Side:
        SCC and Intergranular Attack
        Localized Wastage and Pitting
        Mechanical Damage
B. <u>Tube Support Plate</u>
        Corrosion
        Deformation
C. <u>Piping and Vessel</u>
        Fatigue
        Corrosion

The steam generators in most PWR's that have operated for more than a year have experienced one or more of these phenomena. The interests of the NRC in these phenomena are shown in Table 2, as we understand them to be.

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Table 2
NRC Interests in Steam Generator Degradation

1. Is it safe to return a degraded steam generator to service?
2. Do we understand the degradation mechanisms and proposed remedial actions well enough to determine it is safe to operate the unit?
3. For how long?
4. How reliable are inservice inspection techniques for identifying the nature and extent of the defects?
5. Is the degradation that occurred likely to be affecting other units? If so, what actions should be required of other licensees to ensure their continued safe operation?
6. What actions should be required of applicants for licenses to minimize the risk to safety, based on our understanding of past experience?

The purpose of this paper is to describe the problems that have occurred in terms of these interests, indicating where possible, what research is being (or needs to be) performed to meet these objectives.

In the design and licensing of PWR's, minor steam generator tube leakage was anticipated, leak detection and tube inspection were provided for, and such leakage was not considered a major safety concern in itself. However, widespread degradation that could lead to major leakage developing from failure of a number of tubes during a design basis accident, resulting in a significant release of radioactivity to the environment, is a potential safety concern. As nuclear plants get older and degradation processes occur, the NRC needs to assure itself that this latter condition has not been reached. We are, of course, frequently in the gray area between these extreme cases, so that, when degradation and/or leakage develops, careful reviews of the facts and proposed remedial actions need to be made on an ad hoc basis to provide answers to questions such as those listed in Table 2.

Steam generator degradation and suggested remedial actions have been the subject of several recent review articles (1,2,3), including a topical conference sponsored by the American Nuclear Society (4), a draft NUREG (5), and an NRC press release in February 1982 (6). For the purposes of this workshop, therefore, the following summary is intended only to provide a basis for discussing possible research needs for improving performance and safety of PWR steam generators.

TYPES OF STEAM GENERATOR DEGRADATION

Materials of construction of PWR steam generators currently in service in the United States are listed in Table 3. Steam generators currently under construction by Westinghouse and Combustion Engineering have, in addition to design changes, changes in materials, as shown in the table. Since operating experience with nuclear steam generators has, on occasion, shown that a treatment designed to alleviate one problem has introduced a different one, we believe it is appropriate to discuss anticipated concerns over operating steam generators with the newer materials as well as the experience to date.

Attack on Inconel 600 Tubing

As shown in Table 1, degradation of Inconel 600 tubing has occurred from both the primary and secondary sides of the PWR steam generators.

Primary Side Stress Corrosion - Stress corrosion cracking of Inconel 600 tubing originating from the primary side of the steam generator has occurred in service in areas where high residual stresses were present from fabricating the steam generator and in areas where in-service deformation occurred as a result of secondary side corrosion processes (denting). Typical locations of cracks from residual stresses have been short radius U-bends of the innermost rows of tubes in a steam generator, and where the transition zone occurs on a tube that has been partially expanded into the tube sheet hole. The U-bend cracking has primarily occurred on tubes fabricated by Westinghouse over a several year period, although it has also been observed on European plants. It appears to be associated with the details of the bending process. Cracks appear to initiate at a point of maximum gradients in residual stresses. Stress corrosion cracking where tubes are expanded into the tube sheet crevice has occurred primarily in overseas PWR's of the present time. Figure 1(a) and (b) shows typical areas where these cracks have occurred. Where in-service deformation has resulted from denting, there has been an accelerated tendency toward primary side SCC. The most significant leak developing from this cause occurred at Surry, as a result of ovalization of a short-radius U-bend, resulting from denting, as sketched in Figure 2.

Figure 3 is an often repeated sketch (7) showing the synergistic interplay of environment, material composition, and stress that underly all SCC phenomena. An NRC sponsored research program is underway at BNL (8), the purpose of which is to develop a sufficient understanding of the degradation mechanisms and causative factors to permit an estimation of the lifetime of a steam generator tube. Results to date have been encouraging that these goals can be met, the principal observations are summarized in Table 4. It is anticipated that by the end of 1983, the program will be completed to a point where predictions of the life time of tubing under a variety of operating conditions can be made, including the situations where active deformation of the metal continues, where deformation has occurred but has been arrested, and where abnormal water chemistry might be encountered with or without active deformation.

With regard to solutions to the problem, returning again to Figure 3, the environment, at least on the primary side of a PWR steam generator, probably cannot be changed at the present time. The material can be changed only in new plants; for all SG's manufactured after approximately 1980, the Inconel 600 tubing has been given a heat treatment to improve its resistance to primary side SCC. On an existing generator, the only variable that can conceivably be modified is the stress pattern, and research is underway at the present time, under the auspices of the Electric Power Research Institute Steam Generators Owners Group (EPRI-SGOG), to develop techniques for in situ stress relief, particularly in those areas where the tube is expanded into the tube sheet.

TABLE 3

STEAM GENERATOR MATERIALS

SECONDARY SIDE	
Vessel	Carbon Steel
Tube Sheet	Carbon Steel
Tubes	Stainless Steel Inconel-600 Incoloy-800
(Tube Support Plates)	Carbon Steel Ferritic Stainless Steel
PRIMARY SIDE	Inconel-600 Stainless Steel

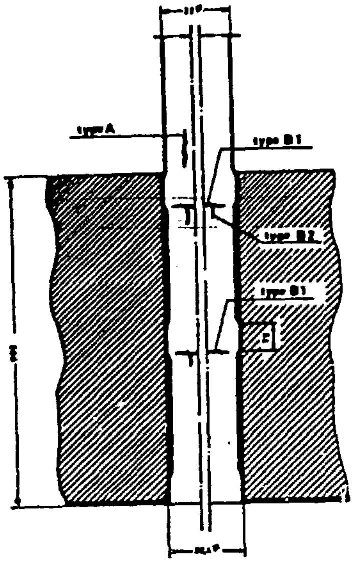

FIGURE 1A: SCHEMATIC OF TUBE-TUBE SHEET AT OBRIGHEIM, SHOWING LOCATION OF PRIMARY SIDE SCC (TYPE B) AND SECONDARY SIDE CAUSTIC SCC (TYPE A)

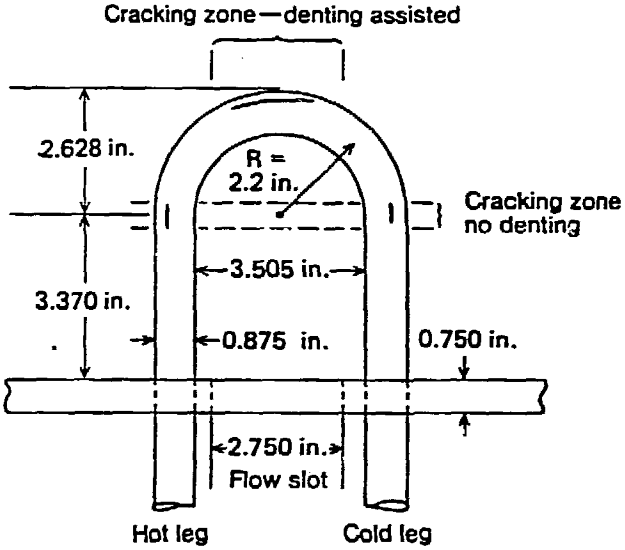

FIGURE 1B: SCHEMATIC OF U-BEND, SHOWING WHERE PRIMARY SIDE SCC HAS OCCURRED

TABLE 4

RESULTS OF BNL INCONEL-600 PROGRAM

1. Wide heat-to-heat variation in susceptibility
2. Strain-rate effects
3. Accelerating effects of cold work
4. Coupling with C steel
5. Effect of H_2
6. Effect of Alloy composition

Intergranular Attack from the Primary Side has occurred in one unit during an extensive layup period in which the upper portion of the (once-through) steam generators were vented to the atmosphere, and small amounts of sulfur were present in the solution, presumably originating from traces of thiosulfate present in the containment sprays of the affected unit. This intergranular attack appears to be accelerated by stress. Research is presently underway under the auspices of the affected utility to determine whether or not it is safe to return the unit to service with tubes in it that have been exposed to this environment. Bench tests performed at BNL have shown that the phenomenon can be reproduced in extremely dilute thiosulfate solutions in the presence of oxygen, and that increasing the amount of Li_2O, reducing the thiosulfate in the solution and eliminating oxygen in the primary coolant can inhibit further attack. The main solution to this problem in terms of Figure 3, therefore appears to be in adjusting the environment. The situation, however, for the affected utility is still under active review by the NRC regulatory staff and their consultants.

Secondary Side Corrosion - Most of the damage to Inconel steam generator tubing from service exposure has occurred on the secondary side, and three of the four largest primary to secondary inservice leaks have originated from secondary side degradation processes. The need to boil water to produce steam creates a mechanism for concentration of impurities against a hot steaming surface and also creates a highly agitated environment in which mechanical damage from foreign objects is a distinct possibility. The need to support the tubing to prevent vibration also inevitably creates creviced areas where impurities can concentrate due to the boiling process; the concentrated impurities may precipitate as boiler scale on the tubes, accumulate on the tube sheet as a pile of sludge, or, where highly soluble, redissolve when the heat flux is reduced.

Impurities that have caused corrosion of the Inconel tubing in these creviced areas fall into several types: first, caustic (NaOH, KOH), which can develop by hydrolysis of carbonates and nitrates of sodium or potasium that leak in through the condenser or by hydrolysis of sodium phosphates intentionally added to buffer condenser inleakage; second, acid phosphates (typically $Na_xH_yPO_4$) where the Na/PO_4 molar ratio is less than 2.3) can where concentrated in crevice areas react with the Inconel to produce complex sodium-nickel phosphates; third, chloride ions inleaking through the condenser (especially when accompanied by oxygen and a cation such as magnesium that hydrolyzes to produce an acid chloride solution) can concentrate in crevice areas to produce local corrosion (pitting) of the Inconel or local corrosion of the tube support plate; and fourth, acid sulfates, which can be produced by thermal decomposition of cation resin beads in the steam generator.

Caustic Stress Corrosion Cracking - The majority of instances of caustic SCC have occurred in the sludge pile area, above the tube sheet, on plants that used a phosphate treatment, where hydrolysis reactions between the phosphate and corrosion product oxides led to the development of free sodium hydroxide in the sludge pile area. This type of attack can be minimized by appropriate water chemistry controls to eliminate the build up of free caustic in the sludge pile. Phenomenologically, caustic stress corrosion appears to

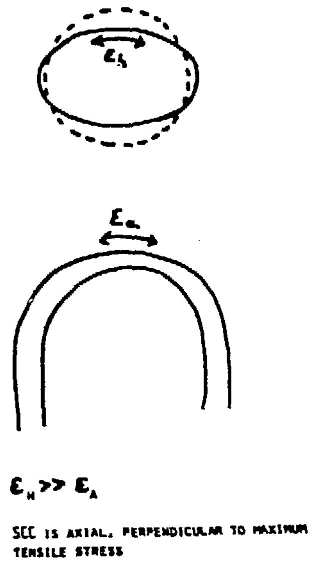

FIGURE 2: SKETCH OF OVALIZATION AT TOP OF U-BEND THAT OCCURS WHEN MOTION OF TUBE SUPPORT PLATE, RESULTING FROM DENTING, DECREASES THE DISTANCE BETWEEN THE HOT AND COLD LEGS

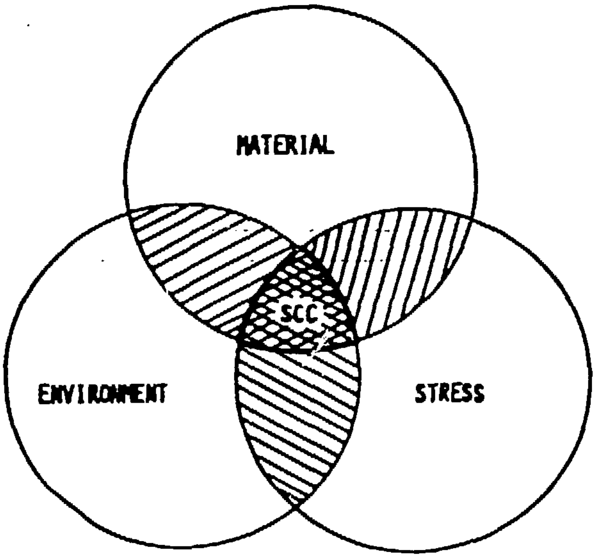

FIGURE 3: SKETCH OF THE INTERPLAY OF STRESS, MATERIAL, AND ENVIRONMENTAL FACTORS THAT CAUSE SCC

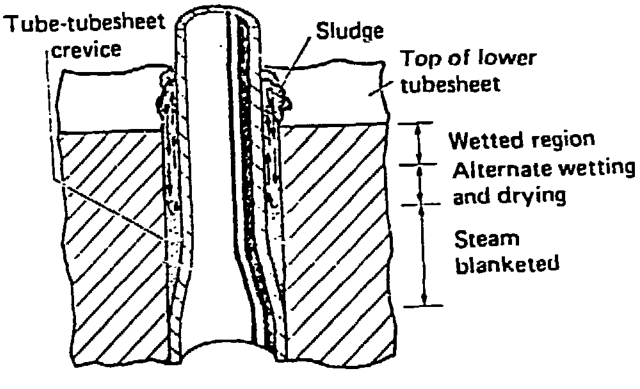

FIGURE 4: TUBE-TUBE SHEET CREVICE

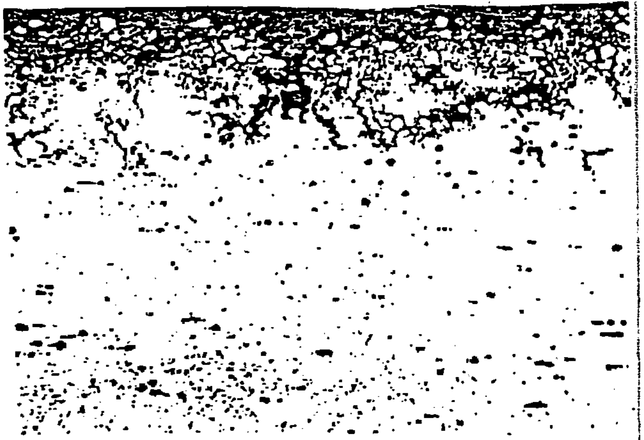

FIGURE 5: NATURE OF IGA ON SECONDARY SIDE OF TUBES IN THE TUBE-TUBE SHEET CREVICE

be quite similar to the primary side (pure water) stress corrosion, in that the same conditions of the Inconel tubing that make it susceptible to one type of attack make it susceptible to the other. The use of thermally treated Inconel tubing to minimize primary side SCC should also minimize secondary side caustic SCC.

Intergranular Attack -- In many older operating PWRs, the tubing is only expanded partially to the tube sheet crevice, as sketched in Figure 4. In some instances, the development of a caustic-forming environment in these crevices has led to a general intergranular attack on the Inconel tubing. A typical example is shown in Figure 5. This phenomenon has been observed in units that utilized a phosphate water chemistry (San Onofre-1), that developed a caustic environment following conversion of phosphates to an avt chemistry (Point Beach units 1 and 2), or in units utilizing an avt from startup, following leakage of caustic forming impurities (Beznau-1 in 1968). In terms of the NRC interests, itemized in Table 2, this has been one of the most difficult forms of degradation to evaluate. Research under EPRI sponsorship is just now beginning to develop an understanding of the degradation mechanism. From a safety point of view, any leaks that develop in the tube to tubesheet crevice area are likely to be small and detectable. The crevices themselves are tightly packed with corrosion product oxides, which tend to limit the rate of leakage. Further, the tube sheet crevice will restrain the tube and prevent either a fish-mouth type opening or a double-ended tube rupture. To date this type of degradation has not been observed to have progressed above the tube sheet into the sludge pile area, where the tubes (or leakage) would not be restrained. The situation in affected units, however, bears watching and requires frequent inspections to ensure that an unsafe situation has not been reached. Based on laboratory tests, Inconel tubing that has been thermally treated to improve its stress corrosion resistance to primary coolant and secondary side caustic SCC also appears to have improved resistance to intergranular attack. Several utilities have performed an extensive sleeving of the affected areas with a more corrosion resistant material in order to minimize the primary to secondary leakage from the source and the chance that an unsafe situation might develop. The newer units utilize the thermally treated Inconel tubing and have eliminated by design the crevices in which this attack has occurred.

Wastage - General corrosion of the Inconel tubes in creviced areas by acid phosphates, which was a matter of some concern in the early to mid seventies, has largely been eliminated by the abandonment of phosphate water chemistry on all but two operating PWR's. Figure 6 shows the general nature of this attack. Complete removal of the phosphates however, has been difficult to achieve, and phosphate residues in the blow-down from some affected units were observed for several years following abandonment of this treatment. On the two units that continue to utilize the phosphate treatment, careful control of sodium to phosphate ratio has prevented significant further instances of either caustic corrosion cracking or rapid wastage. However, some units still in operation have many previously-plugged tubes containing defects similar to that shown in the figure. One unit (Palisades) attempted a program of sleeving to increase the residual strength of the tubing in the wasted areas.

Pitting - Pitting of Inconel tubes has occurred on several units where a combination of oxygen or air inleakage through the condenser, chloride inleakage, and copper ions has set up local corrosion cells. Typically, the pits are observed as rows of small diameter penetrations. Mechanical tests suggest that these pits, while they may lead to primary to secondary leakage, cannot seriously weaken the rupture strength of the tube. They can however, be a significant operational problem and, since any primary to secondary leakage is matter of some concern to the NRC, they may require frequent shutdowns of the affected unit. Pitting by chlorides can be controlled by improved condenser performance both for the elimination of the condenser as a source of chloride, and (perhaps even more importantly) as a source of oxygen to the system.

Pits of the type described have occurred in operating units in an area away from the tube support plates. Where the same species that cause pitting on a free tube surface get concentrated in the tube to tube support plate crevice, denting type reactions, i.e., corrosion of the carbon steel support plates, have predominated. In these areas the carbon steel plate probably provides galvanic protection against pitting of the Inconel. In units currently being designed with stainless steel tube support plates, the denting type reactions are prevented, and pitting type reactions will probably prevail in these crevices, should the same combinations of impurities enter the steam generator.

Pitting also has been observed where condensate demineralization was used to protect the steam generators from intrusion of impurities from the condenser. Resin fines are known to hydrolize to form acid sulfate impurities at steam generator temperatures. Should these resin fines concentrate or get trapped in a tube to tube support plate crevice, a localized pitting of the Inconel will occur.

Mechanical Damage - Mechanical damage to the secondary side of steam generator tubes can arise from several sources. Tube to tube-support plate impact has not been widespread to date , although vibrating flow baffles have caused some wear of Inconel tubing in the preheater sections of one or two of the newer units. As design changes are made to steam generators to minimize areas where corrosive impurities can concentrate, we may find greater instances of vibration induced degradation. In several of the earlier PWR's, fretting between the tubes and anti-vibration bars was observed. This problem was resolved by changing the design and material of the anti-vibration bars on subseqent units. Mechanical damage (wear) has also been observed near the uppermost tube support plates in once-through steam generators (3). The abrasive agent is presumed to be corrosion product oxides carried in suspension by the high velocity steam.

The largest leaks from mechanical damage have occurred as a result of foreign objects inadvertently left in the steam generators. At one unit, a large spring from a sludge lancing tool was inadvertently left in the steam generator and vibrated against the tube, producing a massive leak. In a second unit (9) a foreign object vibrating against the outermost row of tubes produced a series of small leaks over a several year period. Following the plugging of the affected tubes, the foreign object continued to damage the

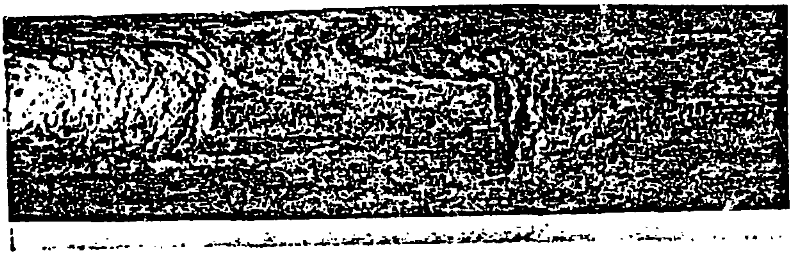

FIGURE 6: Nature of Wastage of Inconel in the Vicinity of Tubing Supports in the Palisades Reactor. The Defect Shown is 35 mils Deep. Flow was from Left to Right.

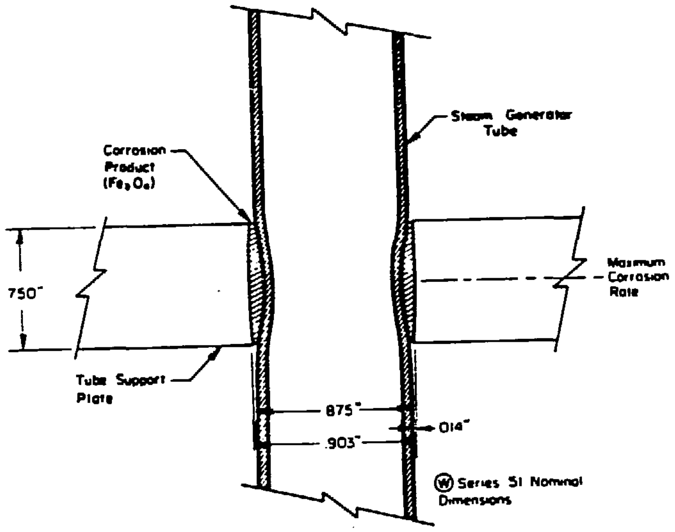

FIGURE 7: SCHEMATIC OF DENTING AT TUBE SUPPORT PLATE CREVICES

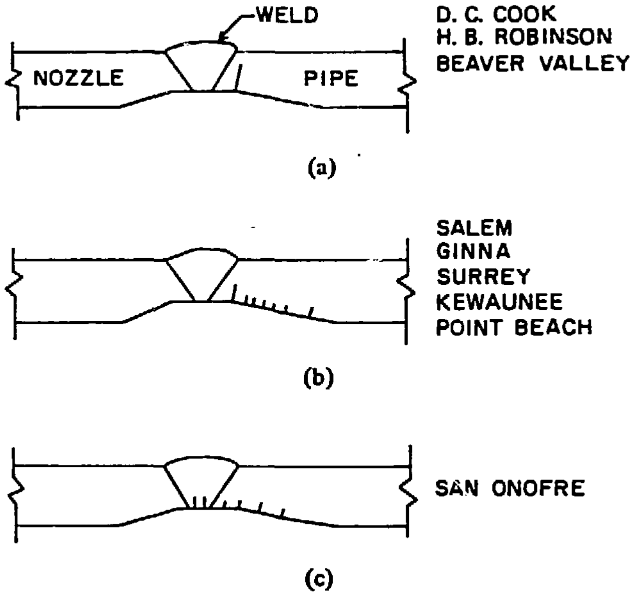

FIGURE 8: Schematic diagram of crack morphology by type and plant: (a) single large crack at root of the notch, (b) several small cracks in counterbore region, and (c) shallow cracks in weld and counterbore region.

previously plugged tubes resulting in their eventual rupture, leaving these tubes free to vibrate against the adjacent tubes in the bundle. Eventually, one of these broken previously-plugged tubes rubbed against a good tube, producing a general loss of thickness over an extended length of that tube, resulting in a fish-mouth type rupture. In terms of the questions in Table 2, the mechanism of this degradation process is, we think, sufficiently understood that it is safe to operate the unit with the foreign objects removed. But the incident does raise the question of whether or not damage might be occurring to previously plugged tubes in other operating units that could lead to these tubes breaking during operation and therefore rubbing and wearing against adjacent tubes. For example, tubes with severe phosphate wastage or through-wall stress corrosion cracks may be continuing to degrade. This is an area which research to date has not specifically addressed, either funded by the NRC or by the industry.

Tube Support Plate Corrosion (Denting)

Denting of steam generator tubes by runaway corrosion of tube support plates was first observed in the middle 1970's and is continuing to the present in some units. Widespread denting and the related problems of inservice strain-induced primary side cracking has led to the replacement of all steam generators at both of the Surry and both of the Turkey Point units. Figure 7 shows a schematic of the denting type reactions. The nonprotective magnetite growth on the carbon steel support plate is known to be triggered by the presence of chlorides, an acid environment, and oxidizing ions such as copper or nickel. In addition to producing dents and deformation in the Inconel tubes, leading to primary side SCC, denting processes result in considerable distortion to and cracking of the tube support plate as well. To date, foreign objects that are capable of damaging tubes have not broken loose from support plates by this mechanism, but the situation bears watching in the future. Although in some units the low pH has been attributed to hydrolysis of residual phosphates, the majority of the acidity is produced by hydrolysis in the steam generator of substances such as magnesium chloride contained in sea water. Thus, plants with condensers cooled by sea water or brackish water are both by experience and prediction the more likely to be degraded by denting processes. The copper or nickel ions that are known to trigger or accelerate denting will not be produced by reaction of these metals with water. Therefore, proper oxygen control or deaeration in the condenser and feedwater lines, as well as in the steam generator, together with careful monitoring of and response to condenser leakage appear to be the best defense against denting reactions. EPRI funded research has shown that chemical treatments involving a mixture of ammonia and boric acid have a beneficial effect on reducing the rate of denting in an affected unit. The effects of this treatment on other components of the system, however, are not clear at the present time.

All secondary side degradation processes (except for mechanical damage) can be controlled or minimized by meticulous attention to water chemistry on the secondary side of the steam generators. The NRC Office of Regulation has issued a Draft Branch Technical Position 5-3 indicating what it believes (given the present state of knowledge) to be acceptable controls for minimizing these degradation processes. The EPRI Steam Generator Owner's

Group has likewise prepared draft recommendations on secondary water chemistry. Were it possible for an operating unit to remain at all times within very tight water chemistry controls, most of these problems could be minimized. Where research is needed, however, is in attempting to develop a sufficient understanding of the interrelations of impurities with crevices in steam generators to permit the placing of acceptable limits on time at which predefined concentrations of impurities can be present before significant damage can be initiated or before crevice corrosion reactions will be triggered that are difficult to stop.

Each design change in either water chemistry or materials that has been made (or is being proposed to be made) needs to be carefully examined in terms of side effects of this change on other aspects of the overall secondary coolant system. For example, lowering the temperature slightly to reduce the rate of secondary side corrosion could throw more impurities into the turbines and potentially increase corrosion problems there, or introduction of demineralizers to protect the system from a leaky condenser has at least in one instance thrown corrosive impurities into the steam generator in the form of resin beads. An older example was the onset of denting type reactions following the abandonment of the phosphate water chemistry treatment. The authors believe that the overall key into future improvement in steam generator performance must come from the proper understanding of the secondary side degradation processes combined with improved design and operational maintainence of condensers to eliminate inleakage of caustic or acid-forming impurities, chlorides, and air into the steam generator and feedwater lines.

Piping and Vessel Cracks

Thermal fatigue processes, possibly accelerated by environmental exposure, have produced cracks and leaks in the feedwater lines to the secondary side of a number of PWR steam generators and in the steam generator vessels themselves at one unit. Figure 8 sketches the type of degradation that were observed on specimens from feedwater lines of a number of units examined in the authors' laboratory(10). The thermal fatigue mechanism arises from the introduction to the steam generator of ambient temperature water from the auxiliary feed system at various stages during startup and shutdown of the steam generators. The obvious solution to this problem comes from proper mixing of the auxiliary and main feedwater to prevent further stratification. Quite recently a similar phenomenon has been observed in the vicinity of the cone to upper cylinder weld on the steam generators at one operating unit. The situation is under investigation at the present time, but phenomenologically the cracks are similar in appearance to those observed in the feedwater lines at several units, especially at San Onofre 1, where environmental effects appear to have been a contributory cause. It is premature at this time to conclude whether residual stresses adjacent to this weld or the thermal stresses from the introduction of cold auxiliary feed water or environmental effects (this unit has suffered considerable denting and pitting and has used a boric acid treatment to retard the progression of denting) or all three of these factors contributed to the cracking and leakage. Research into the relative importance of these three factors on