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DENTING OF INCONEL STEAM GENERATOR TUBES IN PRESSURIZED WATER REACTORS

FINAL REPORT

DANIEL VAN ROOYEN AND JOHN R. WEEKS

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Corrosion Science Group

DEPARTMENT OF NUCLEAR ENERGY BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

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ABSTRACT

Denting is a form of damage that results from the rapid, linear growth of magnetite on carbon steel tube support plates in tube-to-support plate crevices. The pressure of the corrosion products distorts the tubes as well as the support plates.

Although denting was first thought to be confined to those recirculating steam generators that had been converted from phosphate to AVT, it has now also been observed in plants still on phosphate, as well as in some that started on AVT. In some units, slightly abnormal eddy current signals have been observed at the top of tube sheets. No denting has been observed so far in the B&W once-through steam generators. In all, some 14 plants are affected.

The degree of denting in operating steam generators appears to be related to the levels and duration of chloride inleakage. Chloride, however, is not the only active ingredient, and does not seem to give denting until local acid conditions arise; consequently, it may be necessary for soluble copper and/or nickel to be present to "trigger" the denting reaction in certain neutral environments: i.e., cathodic depolarization helps to initiate anodic corrosion in crevice regions. Some cations in solution may also catalyze the formation of magnetite.

Chloride concentrations in actively corroding crevices can increase by several orders of magnitude over the bulk coolant as a result of electrochemical action and local boiling, and it is, therefore, difficult to develop Cl specifications that can be used generally for bulk secondary water. Maintaining Cl low enough to prevent denting may be unmanageable without full flow condensate demineralization in coastal plants with copper alloy condensers and feedwater lines, unless leak-free condensers are used.

Inconel 600 tube defects and leaks were first observed at Surry and Turkey Point, which were severely dented. The cracks originated from the primary side, and were found to be caused by primary side stress corrosion cracking of highly strained tubing. Some minor leaks have subsequently occurred in a few other steam generators. Suggestions are included of work to elucidate the quantitative aspects of stress corrosion cracking.

I OBSERVATIONS OF DENTING

During regular eddy current inspection for tube damage in steam generators at Surry and Turkey Point several months after converting from PO_4 to AVT, it was found that the probe could not be passed through many of the tubes, because they were constricted at tube support plate intersections. Subsequent removal of portions of tubes and tube support plates confirmed that the deformation resulted from carbon steel corrosion products in the support plate crevices. This phenomenon was referred to as "denting". At that time, Surry and Turkey Point units were reported to have been attacked because they (a) had been converted to AVT after prolonged operation with phosphate and also (b) used high chloride condenser cooling water which leaked into the secondary coolant and caused considerable chloride contamination.

A primary to secondary leak of 80 gpm in Surry 2 steam generator led to the discovery of longitudinal intergranular stress corrosion cracking (SCC) at the apices of several tubes, and also at Turkey Point, originating at the primary surface. One of these was through the wall, 4" long, and had caused the (larger) observed leak. The cracking was associated with tube straining which occurred when the legs of the U-shaped region moved inwards due to TSP deformation at flow slots, (so-called "hourglassing"). The inner row of tubes (shortest radius of curvature) was the only one that showed SCC and tubes in this row had the most severe elliptical distortion. All tubes with high strain at the apices, whether cracked or not, were plugged, and involved tubes up to the third row.

Minor leaks were found in the support plate region also. These were inspected and found to be SCC. Several cracks not through the wall were also detected. Leaks were very small, partly because of the presence of high local stress exerted on the tube by the solid corrosion product on the outside. These tubes were also plugged.

Two wedge sections, each including a short length of dented tube, were cut from the top of one of the Turkey Point 4 and one of the Surry 2 steam generator TSP's for laboratory examination. Also, in situ photography was possible of some support plates, including both internal and external tube surfaces. The observations can be summarized:

1. Denting occurred in tube support plate (TSP) regions, where the deformation consisted of non-uniform squeezing inwards of affected tubes. This reduced the I.D. of tubing up to 200 mils in some instances.
2. Primary side intergranular, longitudinal stress corrosion cracking occurred in a few tubes at the U-bend regions with small radius and high deformation, as well as at some of the support plate intersections where large amounts of denting had occurred.
3. The space between a TSP and a dented tube was completely filled with the solid corrosion product, mainly magnetite (Fe_3O_4) so that the tube was "frozen" in the TSP hole.
4. Cracking of the support plate had occurred, and the cracks contained corrosion products. Upon cutting out the wedge samples, a small section of each of the two involved supported plates became dislodged as a result of prior cracking. There have been several cracks through the membrane between support holes and interstitial flow holes.

As a result of the damage at Surry and Turkey Point, plans have been made to replace the steam generators, including the use of tube sheets made of stainless steel, and with a different design for the holes in the support plates. Also as a result of this experience, a careful analysis was made of all other inspection data obtained at other plants, in order to ascertain whether even very minor amounts of "denting" had developed. It is now thought that there may have been very minor indications in some steam generators, undiagnosed at the time, before Surry and Turkey Point problems occurred.

Subsequently, more cases of minor denting were found to be developing, together with observations of intermediate degrees of the same type of corrosion. The Westinghouse and Combustion Engineering nuclear plants are discussed separately below.

Table I lists the most recent denting ratings for Westinghouse plants; note that the latest inspection dates vary for individual units. It should be noted that the indicated degree of denting, for instance "moderate", is included to describe the damage in terms of how widespread it is, how deep the deformation is, if any tubes have leaks, or if there is hourglassing and other damage to the support plates. The most reasonable definitions have been adopted in this report, and a consistent approach to nomenclature has been followed.

Yankee Rowe and Indian Point 1 are not included in the Table of Westinghouse plants, because both are small and the latter is no longer operating. Both of these plants have stainless steel steam generator tubes, and both are presumed to have had enough Cl^- ingress to cause some SCC problems. However, no denting has been reported in either unit, suggesting that the Ni-content of the steam generator tubes may be one of the factors related to denting. It is difficult to tell how significant this observation is, however, because concern over the Cl^- cracking of stainless steel may have affected plant operations so as to maintain very low Cl^-, which would be very beneficial. Also, design differences between the older, smaller units and the more recent Westinghouse and CE steam generators may have played a significant role.

Apart from Surry and Turkey Point, the only other "extensive"* rating by Westinghouse is for San Onofre (October, 1976), which is still on phosphate. Denting here has caused some leaks and hourglassing, but is confined to the bottom support plate; for this reason, i.e. lack of widespread denting, the "extensive"* rating is not the same as for Surry or Turkey Point. H.B. Robinson 2 is also still on phosphate, and is thought to be slightly dented, although this needs confirmation. Both of these plants may have had a period of inadequate phosphate addition, which could have started denting. However, in view of the extremely low Cl^- level of the cooling water at Robinson, it is possible that the phosphate addition could be implicated

* It is suggested that the present degree is better described by "moderate" and that this should be used in future unless the denting becomes worse.

TABLE I

INCIDENCE OF DENTING

WESTINGHOUSE PLANT COMPARISONS

PLANT	MOS. ON PO_4	MOS. ON AVT	MOST RECENT INSPECTION	DENTING	LEAKAGE AT DENTS	CONDENSER COOLING WATER
SURRY 1	29	27	04/77	Extensive	Yes	Brackish
SURRY 2	23	26	03/77	Extensive	Yes	Brackish
TURKEY POINT 3	23	31	11/76	Extensive	Yes	Sea
TURKEY POINT 4	14	31	11/76	Extensive	Yes	Sea
SAN ONOFRE	107	0(?)	10/76	Extensive*	Yes	Sea
INDIAN POINT 2	33	25	04/77	Moderate		Brackish
POINT BEACH 1	47	30	10/76	Moderate	No	Lake
POINT BEACH 2	28	30	03/77	Moderate		Lake
RINGHALS 2	4	29	04/77	Moderate	No	Sea
ROBINSON 2	81	0	11/76	Minor or none	No	Lake
BEZNAU 2	34	32	08/76	Minor	No	River
GINNA	60	29	04/77	Minor	No	Lake
CONN YANKEE	96	22	06/76	Minor	No	River
DOEL 1	3	30	03/77	None**	No	Sea (FFCP)
DOEL 2	0	21	12/76	None**	No	Sea (FFCP)
D.C. COOK 1	HF	27	02/77	None**	No	Lake
TIHANGE 1	0	26	12/76	None**	No	River
BEZNAU 1	33	33	06/76	None	No	River
ZORITA	115	0	03/77	None	No	River
MIHAMA 2	21	17	07/76	None	No	Sea
MIHAMA 3	0	15	(06/77)	-	No	Sea
TAKAHAMA 1	6	23	02/77	None	No	Sea
TAKAHAMA 2	HF	28	10/76	None	No	Sea
GENKAI 1	0	27	11/76	None	No	Sea
KEWAUNEE	6	30	01/77	None	No	Lake
ZION 1	21	25	03/76	None	No	Lake
ZION 2	11	29	01/77	None	No	Lake
PRAIRIE ISLAND 1	10	30	03/77	None	No	River
PRAIRIE ISLAND 2	HF	28	10/76	None	No	River
INDIAN POINT 3	0	13	(03/78)	-	No	Brackish
FESSENHEIM 1	0	1	(03/79)	-	No	River
TROJAN	0	16	(05/77)	-	No	River (FFCP)
SALEM 1	0	5	(11/78)	-	No	Brackish
BEAVER VALLEY 1	0	12	(11/77)	-	No	River

( ) Not yet available.

* But not as widespread as Surry and Turkey Point, suggest "moderate" for future use.

** Incompletely interpreted abnormal signals at tube sheets - see text.

HF Hot functional test only.

FFCP Full flow condensate polishing.

during prolonged operation, since one source[1] reported it to be capable of disrupting the protective magnetite layer on the carbon steel, but if this is so then it is most difficult to explain the absence of observed denting during the years that phosphate was the preferred secondary water treatment of almost all plants.

Point Beach 1 and 2 use Lake Michigan water, and are moderately dented. Both had extensive prior operation with phosphates before changing to AVT. Their Admiralty condenser tubes have leaked, and there are now partial stainless steel sections. Since the onset of denting, they have adopted an upper limit of 0.15 ppm Cl^- in the blowdown, and first tentative indications are that denting is slowing down. There are no details yet how far below 0.15 ppm Cl^- has actually been kept.

Of the moderately dented steam generators, Ringhals 2 (seawater cooled) is exceptional because it had very limited time on phosphate (4 months) before conversion to AVT, and the PO_4 period included little power operation. Observations at this plant point to the fact that quite low bulk Cl^- may be harmful, because there was no denting in mid 1975, while 2 to 6 mils diametral deformation was found on every hot leg intersection in April, 1977, with a small amount of hourglassing of the rectangular flowholes. Available data for Ringhals 2 show that it had maintained less than 0.1 ppm chloride in the blowdown except for about 5 excursions, and the plant operated out of specification only 19 days since November, 1976, with the chloride being <1 ppm during these 19 days. Furthermore, Ringhals 2 had very few condenser problems during phosphate operation. Tubes and a wedge of tube plus support plate will be cut out and examined to get more facts and to try and find out if phosphate is involved in this denting, but in view of the Maine Yankee denting (started AVT, see below) it is doubtful if this point will be resolved beyond any reasonable doubt.

Minor denting was indicated at Robinson 2, Beznau 2, Ginna, and Connecticut Yankee. No hourglassing has been seen at any of these plants. The 3 U.S. plants will be discussed in more detail in the group of "fresh"-water plants, and cracking at Ginna will be treated separately.

A new category including Doel 1 and 2, D.C. Cook, and Tihange 1 appear to fall in a "grey" area since anomalous signals were obtained in the region at the top of tube sheets; the type of eddy current signal seen at these plants is somewhat different from the classical denting signal, but it may well be that some distortion is occurring.

At D.C. Cook 1, phosphate was used for hot functional testing, but AVT has been used since initial criticality. The plant has arsenical copper condenser tubes, and uses Lake Michigan water. Eddy current signal aberrations at the top of the tube sheet were reported for about 50 tubes on steam generator 3. Signal aberrations are susceptible to interpretation as very shallow wall loss or as some sort of mechanical distortion of the tube, e.g. minor ovality or denting. Minor variations were noted in the signals obtained in April, 1976, and February, 1977. Several new indications also were noted in 1977. No ECT indications were obtained at tube support plate intersections.

The Doel plants are seawater cooled with aluminum brass condenser tubing. They are equipped with full flow condensate polishing, consisting of two parallel systems, which can be turned off one at a time for regeneration. Each has a cation bed followed by a mixed bed, with a 10% bypass. Doel 1 had about 3 months operation with phosphate, while Doel 2 started up with AVT. After 3 cycles at Doel 1, and 1 cycle at Doel 2, abnormal signals have been observed in all the steam generators at the top of the tube sheet (hot leg) in the sludge zone. Signal increases were noted between the 1976 and 1977 inspections at Doel 1. These signals are found only in tubes with sludge deposits around them. There is a 3 to 5 inch sludge pile on the hot leg side. If interpreted as dents, the apparent magnitude is less than 0.5 mils. The frequency analysis of the signals indicates a non-symmetrical effect. Only a few such signals have been seen at one support plate in one steam generator. Many outages occurred at Doel because of condenser leaks. They now have retubed the condensers. At one point, resins were pumped into the steam generator from an unused Powdex system; breakdown of resins a high temperatures normally creates an acid environment.

Tihange 1 was started up on AVT and has river water for condenser cooling. Although signals similar to those at Doel have been reported, no further details are available.

A long-term comparison of several of the U.S. "fresh"-water plants, listed in Table II, should provide valuable information, since they cover a spectrum of conditions but still retain some common factors. An analysis of this type is very difficult, though, without an intimate knowledge of plant operating procedures; variations in procedures mean that corrosion caused by a Cl^- "incident" will differ from one plant to another, depending on how quickly it is removed, and what other metal ions were present. Also, the long-term observations may be affected by measures that are adopted to prevent or arrest denting.

So far, only trends can be observed, but they are probably very significant. It is evident that there is a strong association between denting and Cl^- contamination; in addition, it appears that even low bulk Cl^- can be harmful in service. It is also likely that prior phosphate is detrimental and that dissolved copper in the secondary water may be involved in starting the rapid magnetite reaction in plants using AVT. More details are discussed below.

Ignoring the doubtful signal from D.C. Cook for the moment, it appears that the dented units used PO_4 for 28, 47, 48, 60, 81 and 96 months before switching to AVT. Those not dented used phosphate for 21, 11, 10, 6 and 0 months. It is unlikely that there is a real cut-off between the closest levels in the two groups, i.e. between 21 and 28 months of PO_4 operation: more probably, the data are the beginning of a trend in which shorter times in prior PO_4 will correlate with less denting rather than no denting, other factors being assumed equal. Unfortunately, many factors are not equal, for instance the dented plants generally have longer total operating times than the non-dented ones, i.e. 58, 77, 81, 89, 90, 118 months, as against 28, 36, 40, 40, 46 months respectively for the two groups. However, the distinction between Point Beach 2 and Zion 1 (58 and 46 months) is too small to be significant. Also not equal are feedwater and condenser materials, condenser

TABLE II

TWELVE NON-SEA-WATER U.S. PLANTS

PLANT	MONTHS PO_4	MONTHS AVT	DENTING	COOLING WATER	CONDENSER
Palisades (CE)	48	42	Widespread, mostly 1-2 mils, max. 4 mils	Lake Michigan*	Admiralty changed to 90-10 Cu-Ni
D.C. Cook	hot test only	27	?**	Lake Michigan	Arsenical copper
Point Beach 1 (W)	47	30	Moderate	Lake Michigan	Admiralty, with stainless steel sections now
Point Beach 2 (W)	28	30	Moderate		
Zion 1 (W)	21	25	None	Lake Michigan	Stainless Steel
Zion 2 (W)	11	29	None		
Kewaunee (W)	6	30	None	Lake Michigan	Admiralty and 304 SS
Ginna (W)	60	29	Minor	Lake Ontario	Admiralty
Prairie Island 1 (W)	10	30	None	River	Stainless Steel
Prairie Island 2 (W)	hot test only	28	None		
Connecticut Yankee (W)	96	22	Minor	River	Admiralty
Robinson 2 (W)	81	0	Minor or None	Lake	90-10 Cu-Ni

* At Palisades, Cl^- levels are about 10-15 ppm in the Lake Michigan cooling water. Palisades plant, itself, uses cooling towers, where evaporational losses will increase the Cl^- levels.

** Some questionable signals at top of the tube sheet.

performance and plant operating procedures. All of these are important, as discussed below in the section on mechanisms.

Hydrogen analyses appear to be very useful in following the denting process, since the rapid corrosion of carbon steel is an anodic process accompanied by the equivalent cathodic evolution of H_2. This method has been used to show, for instance, that Turkey Point (extensively dented) produces relatively high amounts of H_2. H_2 levels may perhaps also indicate finer differences between non-dented units, as well as others with minor, moderate or extensive denting: Hydrogen generation by corrosion at Turkey Point 4 was 14 times greater than that at Prairie Island 1; at Kewaunee, it was 2 to 3 times greater than at Prairie Island 1; at Indian Point 2, hydrogen levels cycled from the Kewaunee level to the Turkey Point level. During an 0.1 gpm primary to secondary leak, hydrogen generation was reduced to almost zero. At that time, the primary coolant contained 175 ppm boron and 0.5 ppm lithium. In a test, boric acid and lithium hydroxide were injected into the steam generator to give a similar chemistry, and again hydrogen generation decreased to nearly zero. To obtain additional data, a series of tests using lithium borate additions was initiated at Surry. In laboratory experiments, Westinghouse has reported similar beneficial effects of boric acid on denting. Obviously, some pointers from the "fresh"-water plants implicate the state of the secondary water and of "poor" condenser performance:

1. Point Beach and Palisades have retubed at least in part, indicating relative difficulties and the possibility of greater Cu^{++} as well as inleakage (Cl^-).
2. Zion and Kewaunee, for instance, have been reported* to be meticulous about maintaining good secondary water and condenser integrity (leak repairs) - they have so far encountered no denting. At Kewaunee, an increased blowdown capacity was provided (up to 90 gpm) so as to maintain good secondary water chemistry. This is reminiscent of a

* Telephone discussion with NRC representatives. See also a similar possibility at Millstone 2, later in this report.

verbal report on Mihama** where there is no denting and great care to ensure good condenser performance. Zion is believed to be plagued by boron leakage into the secondary coolant, which may in part be responsible for the absence of denting, in view of the preliminary findings on the beneficial effects of boric acid. It should be kept in mind that Zion has stainless steel condenser tubes.

3. The denting at Point Beach may have been slowed by the adoption of very strict procedures to ensure low Cl^- levels.*

4. It is suggested that AVT may possibly increase the aggressiveness of the condensate to Cu-base condenser tubes; if so, increased Cu^{++} in solution would be adverse in the presence of Cl^-.

5. Prairie Island, with good secondary water, and stainless steel condenser tubes, has no denting in either unit, one of which had 10 months on phosphate, followed by 30 on AVT, and the other without phosphate operation. The use of stainless steel condenser tubes is a common factor with Zion, which also has no denting, as stated in "2" above. Lake Michigan water has about 10-15 ppm Cl^- (Zion), while the Mississippi river at Prairie island has about 5 ppm Cl^-, which makes the cooling water at these two plants approximately similar from the Cl^- standpoint.

Three Combustion Engineering plants are now known to have been "dented". Palisades, a $PO_4 \rightarrow$ AVT converted unit, with Lake Michigan cooling water, and cooling towers, was reported earlier, but operation at the other two has

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* Telephone discussion with NRC representatives. See also a similar possibility at Millstone 2, later in this report.

** Telephone discussion with EPRI (T.O. Passell).

been totally on AVT; they are Maine Yankee (brackish water) and Millstone 2 (sea water). Most of the support plates in both units are of the egg crate design, with only 2 partial support plates, of the drilled hole design. The Maine Yankee plant has 90-10 CuNi condenser tubes, while Millstone 2 has Al-brass. The main condenser at Millstone 2 has given such poor performance it has had to be retubed. The denting at Maine Yankee is limited to the drilled hole partial support plates, but at Millstone an inspection in late 1977 showed some dent-like signals also at places within the egg crate region. The Maine Yankee plant started up October, 1972; in July, 1973, steam generator 3 was inspected. Only a few tubes in the partial drilled support plate were examined at that time. No damage was found in any tube. In July, 1974, steam generators 1 and 2 were inspected, with the same negative result. In June, 1975, steam generator 3 was inspected for the second time. No damage of any kind was seen, although only a few tubes in the partial support plate were examined. At this time, sludge was present on the tube sheet, up to 3 ½ inches deep. In May, 1977, steam generators 1 and 2 were examined, with relatively shallow dents found in the drilled partial support plates, averaging about 1 mil. Sludge on the tube sheet has reached a maximum depth of 4 or 4 ½ inches over a few tubes with a little more in the hot leg than in the cold leg, but no sludge was found on the drilled support plates. The partial drilled-hole support plates are at the 7th and 9th support levels with a total of about 30% of the tubes passing through one or the other or both of them. Radial clearance in the drilled holes is 8 mils by design.

The inspection results are shown in the following Table:

TABLE III

MAINE YANKEE INSPECTION RESULTS

Steam Generator		No. Tubes Inspected SP7	No. Tubes Inspected SP9	No. Tubes Dented SP7	No. Tubes Dented SP9
1	hot leg	85	37	25	5
	cold leg	85	37	2*	0
2	hot leg	113	31	19	0
	cold leg	113	31	1	0

*to be confirmed

At Maine Yankee, Cl^- and cation conductivity are monitored in the condensate and Cl^- is checked daily in the steam generators. Minor condenser leaks occurred about once a month. When Cl^- exceeded 0.05 ppm in the condensate, power was reduced, and the leak located and fixed in 1 to 1 ½ days. Generally, therefore, secondary water quality was controlled and maintained, although 1 ppm Cl^- in the blowdown was exceeded about 60 times over the entire life, and, on a few occasions early on, rose to some tens of ppm's for short periods. On the one hand, their experience is disturbing, because denting occurred in spite of their efforts to keep the secondary water clean. On the other hand, denting at Maine Yankee in 53 months is much less serious than in 23 months at Millstone 2, where condenser problems were more severe, as outlined below.

TABLE IV

THREE COMBUSTION ENGINEERING PLANTS

Plant	Months PO_4	Months AVT	Denting	Cooling Water	Condenser
Palisades	48	42	Widespread, 1-2 mils, some 4 mils	Lake	Admiralty changed to 90-10
Maine Yankee	0	53	Only some intersections, about 1 mil, some 4 mils	Very Brackish	Al-brass and some 70/30 CuNi (some retubing)
Millstone 2	0	23	Widespread 7-13 mils.	Sea	Al-brass

At Millstone 2, the initial denting in the drilled plates was widespread, measuring 7-13 mils, but no leaks were found in the steam generator tubing. This plant has had a relatively high level of Cl^- (and presumably Cu^{++}) in the secondary water, because of almost continuous low level inleakage through the condensers. The Millstone 2 plant started in August, 1975. The Al-brass main condenser has already been retubed, which is a general indication of their condenser troubles. A minimum of .15 ppm Cl^- has been reported, with a typical blowdown analysis in 1976 of:

Na	0.2 ppm
Cl	0.6 ppm
Conductivity	6 μmho/cm (total)

Contamination was only a little less in the first part of 1977. Since startup, Cl^- has exceeded 1 ppm in 76 days. Added to this, concentrating factors could multiply Cl^- to several thousand ppm in crevices.

Initial data for steam generator 2 showed all intersections with the #10 and #11 support plates had indications, i.e. all 167 tubes examined. As stated above, deformation ranged from 7 to 13 mils. This experience is consistent with a denting mechanism in AVT units that involves high Cl^-, and possibly copper ions from Cu-base condenser tubes.

In the period between first finding dents at Millstone 2 and a subsequent inspection late in 1977, care was taken to keep the Cl^- levels very low in the secondary water. As a result, it is believed that the rate of denting has decreased, and hope is expressed that it may stop completely under such operating conditions.

The latest inspection at Millstone 2 has now, for the first time, indicated a possibility that there may be some slight denting at the egg crate crevices, but this aspect is yet to be analyzed and will be discussed in a later report if more information is obtained. Also, since these observations were made during a time when denting, at the drilled holes, was getting less (controlled Cl^-), this aspect will require more detailed examination of the inspection data before it can be confirmed and discussed further.

Another finding during the latest Millstone inspection was that there was movement - due to Fe_3O_4 growth - of the drilled tube sheet, causing "squashing" of the tubes. As a result, a plugging program is underway, and remedial measures to avoid further "squashing" are being explored with the hope of early implementation after approval by the Nuclear Regulatory Commission.

II BNL DISCUSSION OF SIGNIFICANT LABORATORY FINDINGS AT WESTINGHOUSE AND COMBUSTION ENGINEERING

A. Westinghouse:

Westinghouse reported data in a 1977 NACE paper,[2] followed by an unpublished verbal description of their continuing laboratory test program later in the year. Details are below.

The carbon steel support plate surface could be up to 27°F hotter than the saturation temperature of the bulk water due to heating in the crevice. (Sea water concentrated by a factor of 10 has a 27°F boiling point elevation.) Coupon immersion tests of carbon steel at 540°F in sea water concentrated 10 fold resulted in rapid corrosion (∿ 7 mils in 20 days). The carbon steel corrosion rate in a crevice between Inconel and carbon steel was lower. Very significantly, the carbon steel plug could be frozen into position by corrosion products, but no Inconel deformation, or denting occurred. With a 10 w/o slurry of the products of corrosion of Inconel in sodium phosphate solution, a negligible corrosion rate was observed. With a slurry of this material in 10 fold sea water, the corrosion rate was approximately double that of 10 fold sea water alone, showing a synergistic effect, but no typical denting reaction, again a very pertinent observation. There was no heat flux in the above tests, but a test with 0.01 fold sea water and CuO could start denting, which slowed or stopped when the CuO was removed, leaving the sea water as corrodent. (See more on this point later.)

In crevice capsule tests, carbon steel plugs were inserted in Inconel tubing, chemicals added, and the capsule sealed and heated. Tube deformation, similar to denting in service, occurred in 0.2 M $FeCl_2$ solution and/or $NiCl_2$ solutions, or with metal phosphate crevice filler in an 0.2 M chloride solution. No tube deformation was noted when 0.1 M NaOH or 0.1 M phosphate ($Na/PO_4 \geqq 2$) were added to neutralize the acidic chlorides. When a nickel-iron-phosphate crevice filler was used, tube deformation (bulging) occurred and metallic nickel was observed at the interface between the carbon steel corrosion product and the crevice-filling phosphate compounds, and chloride was detectable on layers close to the carbon steel. Exposure was in an $NaCl/NiCl_2/FeCl_2$ solution.

In heated crevice tests, an electrically-generated heat flux of 20,000 Btu/hr-ft^2 was used* to generate 20° to 30°F superheat at a saturation temperature of 540°F. Assemblies were run 2 weeks with 500 to 10,000 ppm of $Na_{1.5}H_{1.5}PO_4$. The crevice became filled with phosphate deposits and Inconel corrosion products generated in situ. On exposure to 0.1 fold sea water for 6 weeks, substantial carbon steel corrosion occurred. Nickel metal was observed at the magnetite/phosphate interface, and mostly iron phosphate remained in the original corrosion product. Chloride was observed near the carbon steel surface. In a parallel test, extensive rinsing (2,000 temperature cycles of 10°F), after initial exposure to phosphate, removed more of the phosphate from the deposit and led to greatly reduced rates of carbon steel corrosion on subsequent exposure to 0.1 fold sea water. The crevice did become filled with calcium sulfate and iron oxides.

In a number of other tests of this type, simulated sludge (Fe_3O_4, CuO, ZnO) was put into the bottom of the autoclave. After an initial phosphating and minimal rinse, denting was observed in heated crevices of 4 to 8 mils initial gap (radial clearance) on exposure to 0.01 fold sea water. When the sludge was removed, denting did not progress. In the NACE presentation, confidence was expressed that attack resulted from the presence of CuO.

In summary, laboratory tests showed that concentrated sea water containing cations of Fe, Ni, or Cu resulted in a rapid, linear corrosion of carbon steel. Similar morphologies are produced during denting in the laboratory tests and in the field. As such, the laboratory techniques are being accepted as a way to evaluate solutions to the problem.

In an extension of the programs discussed at NACE, an additional test was carried out with a heated assembly with several crevices. Rapid denting (1 mil/week) was observed in 0.01 fold sea water with copper oxide present in the bottom of the autoclave. When the test was re-started and

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*NOTE Although 20,000 Btu/hr-ft^2 is low or average heat flux in a steam generator, it is high for a crevice region.

run for several weeks without CuO in the vessel, the denting rate gradually decreased to a value hardly measurable. Addition of CuO to a subsequent run caused denting to proceed again. During the time that CuO was present, Cu metal was deposited on test surfaces but the deposit was not removed as the tests alternated between those with and those without CuO.

In capsule tests, as noted earlier, little or no corrosion occurred when acidic chloride solutions were neutralized with sodium hydroxide or phosphate. Several other neutralization methods were considered, with two identified as possibly acceptable for use in steam generators; lithium borate and calcium hydroxide ($Ca(OH)_2$). Capsule tests with aggressive corrodants were run in which bulging was produced, and then repeated with $Ca(OH)_2$ or lithium borate added; no tube deformation occurred in 28 weeks. In other experiments with heated crevice assemblies, denting was started with $CuCl_2$. When $Ca(OH)_2$ was added, the denting stopped, and it did not restart when $CuCl_2$ was again added without $Ca(OH)_2$. A large number of tests remain to be done to qualify any of the possible techniques for controlling denting in operating systems.

Model boiler tests are also being done at Westinghouse, using Inconel 600 tubes with a single, open ended crevice cup of Inconel and two, double open ended support plate crevices of carbon steel. The latter has an 0.012 inch crevice gap, prepacked to 60 to 70% density with Fe_3O_4 of mixed particle size. The primary and secondary temperatures were about 610°F and 522°F, respectively. In one test, the makeup solution contained 0.34 ppm chloride, 0.167 ppm copper, and 2.1 ppm ammonia; after 57 days, 10 mil radial dents were found. This test demonstrates the effectiveness of $CuCl_2$ in causing denting, but does not clarify the role of packed crevices.

B. Combustion Engineering:

Combustion Engineering (CE) has confirmed that denting occurs in the complete absence of any phosphate, which is generally consistent with Westinghouse data and the original findings of Potter and Mann.[3] These CE results, therefore, showed that denting is possible without the PO_4 to AVT conversion, before it was found in service. The details of the CE tests were as follows:

A mixture of 71 parts of magnetite, 12 of copper oxide, 12 of nickel metal and 5 of copper metal was packed inside a crevice around a heated Inconel tube and exposed so that there was some degree of superheat within the 8 mil radial crevice. The bulk water had additions of Turkey Point cooling water to give two levels of chloride. One was 100 ppm and the other was 1 ppm. In the case of 100 ppm, 22 mils of tube denting was observed in 22 days and this could be shown by eddy current testing before dismantling the apparatus. In the case of the 1 ppm chloride in the bulk water the experimental setup was somewhat different, i.e. the "umbrella" around the tube was made of quite thin carbon steel so that it, rather than the tube, became deformed and cracked during the denting reaction in the 56 day test; interestingly, a post-test analysis indicated that Cl^- concentration at the Inconel interface with the corrosion product was as high as 50,000 ppm. These data confirm that more than one condition can be effective in producing porous, non-protective Fe_3O_4. In the CE test, we think that $CuCl_2$ was formed, and triggered denting by producing acid Cl^- in the crevice, as discussed further in the mechanisms section. The role of sea water has to be further clarified, but in view of the absence of denting in the Westinghouse tests with concentrated sea water alone, it is believed that the mechanism outlined above, i.e. $CuCl_2$, is the most likely cause of denting. Future work should try to clarify how combinations of low Cu^{++} and hydrolyzable sea water salts may work in conjunction to casue the denting reaction.

III DENTING MECHANISM

A. General Review:

At the time that denting was first observed in operating plants, experience suggested that denting occurred only in plants that:

(a) had been converted from $PO_4^{\equiv}$ to AVT after prolonged operation with $PO_4^{\equiv}$, and,

(b) used sea- or brackish cooling water and had poor condenser performance.

The denting process appeared to be directly related to reactions described by Potter and Mann,[3] who discussed the formation of "run-away" Fe_3O_4 on steel coupons immersed in high temperature aqueous solutions of hydrolyzable chlorides, specifically $NiCl_2$, $FeCl_2$ or $CuCl_2$, but not NaCl by itself. It can be deduced, therefore, that an acid chloride environment causes the rapid corrosion and denting. The unknown part is, in which way or ways does it happen in service.

Potter and Mann[3] did not use crevices, and did not consider the consequences of the "run-away" Fe_3O_4 reaction in terms of mechanical damage such as has been found in tube denting. However, there is little doubt that tremendously high forces can be generated if corrosion products are constrained. Examples are quoted below, some of which are taken from an unpublished review by J.R. Galvele:

a. N.A. Nielsen[4] (of E.I. duPont de Nemours, Wilmington, Delaware) several years ago suggested a mechanism for SCC which included high stresses resulting from the wedging action of solid corrosion products inside the cracks.

b. As a result of Nielsen's theory, H.W. Pickering,[5] et al measured stresses in the region of 4,000-7,000 psi in stainless steel resulting from solid corrosion products; they also found stresses near the yield point at the base of a notch.

c. Hydrogen, which is also a corrosion product, can cause blistering in metals.

d. Since the early 1960's there has been a number of reports on the spalling of concrete used in bridge construction, as a result of solid corrosion products from steel reinforcing rods. (e.g. R.F. Stratfull[6]).

e. Magnani[7] attributed SCC in uranium alloys to the wedging action of uranium hydride (UH_3) formation, which had a volume of 70% greater than the alloy, and set up high stress fields.

f. Evans[8] reported snapping of steel and aluminum rivets and bolts due to voluminous corrosion products in crevices.

g. Logan[9] provided information on the results of high forces on stainless steel in contact with mild steel when the latter was converted into bulky corrosion products.

h. Logan[9] believed that a case of stress corrosion occurred in a magnesium alloy due to stresses from voluminous corrosion products.

i. Fontana[10] reported failure in cast iron due to wedging effects of corrosion products.

j. Sprowls[11] and Spiedel[12] attributed exfoliation of aluminum alloys to pressure exerted by corrosion products.

k. There are many instances[13, 14, 15, 16] in which very high stresses were measured experimentally for several materials as a result of oxidation in air or oxygen. For instance, tantalum oxidation gave stresses as high as 50,000 to 100,000 psi, and oxide film stresses on zirconium and Zircaloy-2 were 160,000 to 240,000 psi.

l. Dimensional changes due to oxides occurred in the case of fuel element cladding and insulating material in the Dungeness B Advanced Gas Cooled Reactors.[17]

m. Griess, et al[18] at Oak Ridge National Laboratory found expansion of C-type specimens due to the force of crevice corrosion products from 2 ¼ Cr 1 Mo steel. The test environment was hot aqueous NaCl and NaOH, with oxygen present. The BNL Stress analysis group estimates that a pressure of 60-80 psi exerted by the growing oxide would have been sufficient to cause the observed plastic deformation of a C-ring, but this does not mean that the reaction forces are restricted to these low stress levels.

In summary, then, conditions are known which give rise to rapid formation of volumnous Fe_3O_4 on carbon steel, and this is expected to exert considerable force on the walls of any confined space within which it is deposited. The observations made on the tubes and TSP's removed from Surry and Turkey Point are generally consistent with such a mechanism. The "runaway" Fe_3O_4 would be less dangerous under a sludge pile than in the tube-TSP crevice areas because tube sheet corrosion would grow parallel to, rather than perpendicular to the tube surfaces. Tube to tube sheet crevices, however, would be expected to behave similarly to tube to TSP crevices.

There is a possibility that thermal cycles in operating plants could add to the denting damage in one of two ways:

1. If the chemical formation of Fe_3O_4 exerts a large force, the reaction may slow or stop if the electrolyte replenishment becomes restricted; subsequent temperature fluctuations could permit more rapid reentry of liquid so that periodic chemical denting can proceed. (Thermally assisted chemical ratchetting)*.

* This is probably a minor aspect, since the oxide is relatively porous.

2. After chemical reaction fills the crevice area with Fe_3O_4, denting would be aggravated thermally if rapid heating of the tube introduced high expansion forces. (Chemically assisted thermal ratchetting).

Because of the apparent prerequisite of the $PO_4^{\equiv} \rightarrow$ AVT conversion for denting in service, first attempts had the objective of finding a triggering mechanism for rapid corrosion in a crevice region, connected with phosphates. It was felt that there had to be a chemical factor in addition to the physical effects of solid products in the crevice, since sludge would always have been present to restrict the flow in at least some of the tube-to-support plate crevices. All of the converted plants had earlier suffered some degree of tube damage as a result of reaction between Inconel and high concentrations of ortho- or pyro-phosphate. Unbuffered hydrolysis of these sparingly soluble heavy metal phosphate corrosion products could possibly lead to a pH drop inside the crevices when the phosphate treatment is discontinued; this would trigger corrosion of the carbon steel, and the anodic action in a confined local region would preserve the acid pH as well as cause the accumulation of high concentrations of chlorides if present even in small amounts in the bulk solution. This was the basis of some earlier arguments to explain acid chloride formation leading to denting. Analytically, a (Na, Ni, Cr, Fe) phosphate is detected in "denting" tests, at the outside of the Fe_3O_4 layer, seeming to indicate its hydrolysis would not be very acid (due to the presence of Na). However, this compound is found on the outside of the Fe_3O_4, in the very active cathodic region, which would be much less acid, and it is suggested that its composition may have been more acid at an earlier stage, i.e. in the anodic region at the onset of the rapid reaction.

Based on Potter and Mann[3] it was anticipated that an all-AVT system was not necessarily immune to denting, since phosphate, per se, was not even used in their coupon tests which produced rapid Fe_3O_4 growth. Fe, Cr, Ni phosphate merely may hasten the onset of denting in unbuffered crevices. Any one of several other ways to produce acid chloride would have the same end result. It is, therefore, unfortunate but not too surprising that denting has now occurred in plants with little or no prior operation with phosphated secondary water, for instance at the 53-month inspection of Maine Yankee and the 23-month inspection of Millstone 2. The induction time was longer at Maine Yankee, where Cl^- contamination was less than at Millstone 2. It is still too early to tell whether denting of the units that started out on AVT will become as severe as has been found at Surry and Turkey Point. In fact, it may never be known, since operating procedures may be changed and other remedial measures are bound to be adopted as soon as they are available and approved.

The research on the behavior of carbon steel performed by Potter and Mann,[3] using solutions containing $FeCl_2$, $NiCl_2$, $CuCl_2$ and others, reported sporadic results with $FeCl_2$ and $CuCl_2$, but consistent "run-away" Fe_3O_4 formation in solutions containing $NiCl_2$. The recent data from the Westinghouse laboratories now show that, when crevices are present, copper ions together with chloride produce denting consistently; the adverse effects of crevices combined with $CuCl_2$, such as may also be introduced in service through in-leakage and corrosion of Cu or Cu-base alloy condenser tubes, are thus indicated. The denting produced at CE in model boilers also occurred in the presence of CuO and Cl^-.

Tight crevices have been claimed by some to be the main ingredient for denting, but in view of the Westinghouse laboratory data that show no denting in 0.1 fold and 10 fold sea water by itself, i.e. in relatively non-acid and non-oxidizing media, even with "frozen" crevices, it seems that species such as Cu^{++}, $Cu(OH)^+$, or Ni^{++} are needed together with Cl^- to set off denting. In-service implications, such as the relationship between the time to denting in AVT units, and (a), the accumulation of inert sludge and (b), the accumulation of active "denting" ingredients, i.e. hydrolyzable chlorides and oxidizing ions, remain to be clarified. Also, in light of more recent data, the role of PO_4 to AVT conversion requires further examination to establish to what extent phosphates are specifically responsible for the early onset of denting in such units, and to what extent the damage simply resulted from the loss of buffer action.

B. More Detailed Analysis of Mechanism:

The laboratory experiments at Westinghouse contain 3 key items that support the mechanistic aspects above, and these are repeated for clarity:

a. When synthetic sea water was concentrated 10 fold, immersed coupons corroded rapidly at elevated temperatures, and crevices of creviced specimens filled with corrosion products but, importantly, there was no denting in spite of the metals being "frozen" together. Merely filling crevices with solid corrosion products did not cause denting even at high Cl^- concentration. Experiments with solutions initially containing copper ions in 0.01 fold sea water showed that denting stopped or slowed when Cu products were removed, i.e. the Cl^- alone was probably not enough to support denting. (See "c" below).

b. When crevices were present together with Cl^- and CuO (i.e. Cu^{++} or $CuOH^+$) then rapid Fe_3O_4 occurred every time, as opposed to sporadically in $CuCl_2$ in the work of Potter and Mann[3] without crevices.

c. Starting denting with Cl^- and CuO, and then continuing experiments in which restarts alternated with and without added CuO, i.e. leaving everything the same except for the CuO, it was found that denting was gradually reduced or stopped in the runs without CuO, and continued in those with CuO. The deposited Cu remained undisturbed in both types of experiments.

The role of an external oxidizing ion, such as Cu^{++} can be:

a. At reasonably high concentrations Cu^{++} can be catalytic (see below) and in addition, it can depolarize the cathodic reaction and produce elevated Cl^- together with increased acidity in a local creviced region.

b. At lower concentrations it may be merely a catalyst in speeding up the ferrous hydroxide conversion to magnetite, without much change in the oxidation potential.

c. It could be plated out, leaving a metallic surface with low H_2 overpotential.

In the depolarizing sense, the triggering of denting could be analogous to pitting of stainless steel in Cl^-, which can be started at an elevated electrochemical potential, but which, on slightly lowering this potential, continues because of the local acidity and higher Cl^- inside the pit, and only ceases at the "protection potential" in the bulk solution. (See schematic representation in Figure 1). The "protection" level of denting, then is felt to be near the potential at which $H_2O \rightarrow H_2$ polarization curve intersects the anodic curve.

Initially, the cathodic and anodic reactions could be:

$$Cu^{++} + 2e \rightarrow Cu \text{ (metal)}$$

$$Fe \rightarrow Fe^{++} + 2e$$

Inside the crevice, accumulated positive ions will require the migration of negative species, such as Cl^-, to maintain charge neutrality. Therefore, Cl^- in the crevice would increase rapidly, and lower the anodic pH because of hydrolysis of $FeCl_2$:

$$FeCl_2 + H_2O \rightarrow Fe(OH)_2 + 2\ HCl$$

where the strong acid would dominate. Concentration of products due to heat flux would also contribute to denting due to local boiling, since it could

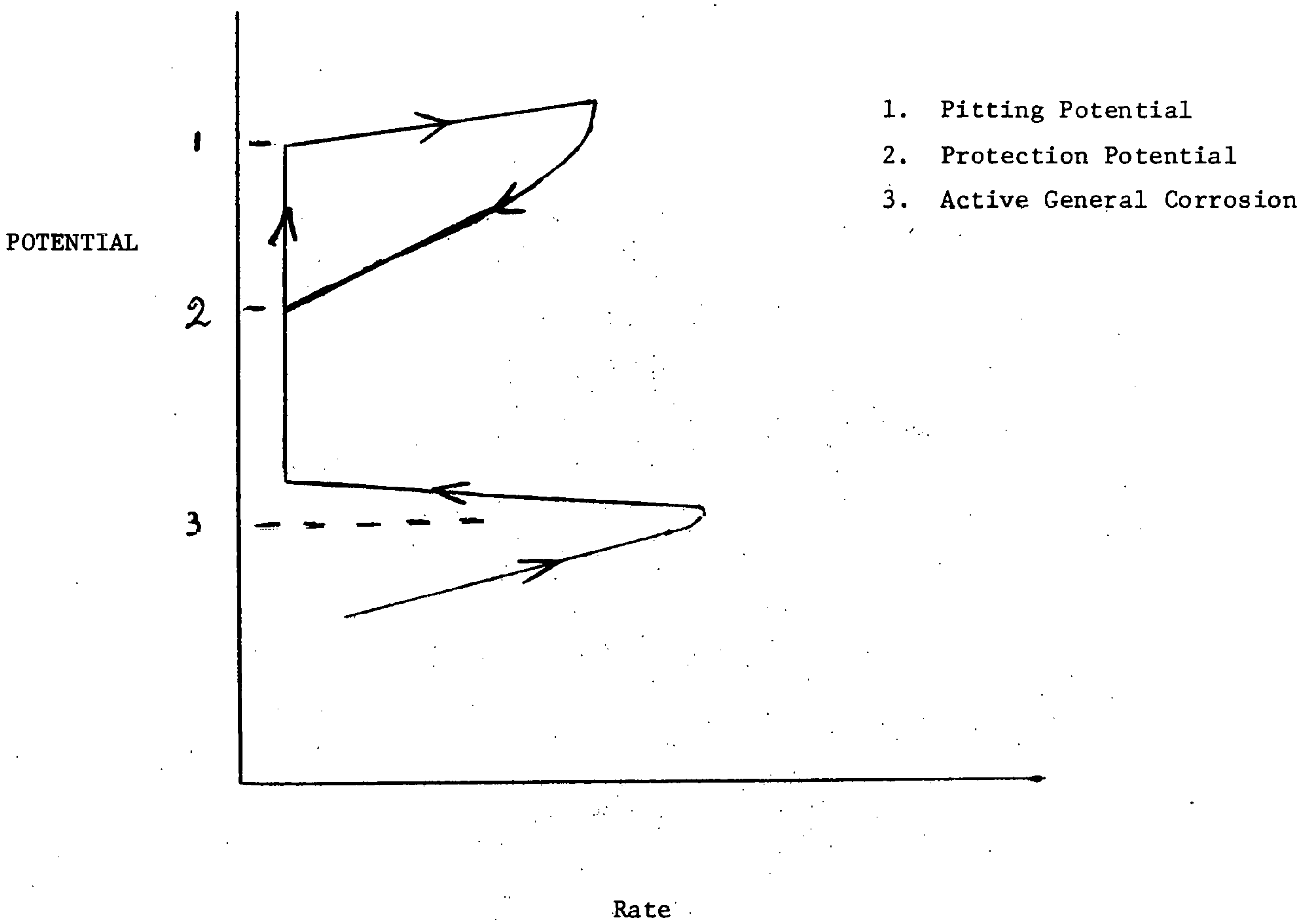

Figure 1

Effect of Potential Changes on Corrosion Rate contribute significantly to higher Cl^- and other salts.

However, there does not seem to be nearly enough Cu^{++} to account for the full extent of denting, and plentiful H_2 is known to accompany the porous Fe_3O_4 formation:

$$4H_2O + Fe \rightarrow Fe_3O_4 + 4\ H_2{}^*$$

This is the reason why it is believed that when present at sufficiently high concentrations, the external oxidizer functions as a "trigger" to create and maintain local acidity. In the laboratory, this process apparently has to be continuous or repetitive, because denting slowed down or stopped when CuO was deleted in a subsequent run. This probably means that H^+ in the crevice solution can become reduced, slowing the Fe_3O_4 reaction, unless there is a low pH solution outside the crevice, or ions, such as Cu^{++} that can react cathodically (outside) so as to maintain the aggressive potential-pH conditions inside the crevice. It is yet not certain that Cu^{++} is present at levels high enough to fulfill such a role under all service conditions, although analyses of Millstone sludge showed substantial amounts of copper. In the above mechanisms, CuO does not act catalytically, in the true sense of the word, since it is not in a regenerative cycle. It seems clear that CuO, not Cu metal, influences the denting reaction in the laboratory, since Cu metal was present in all tests. Furthermore, although Ni^{++} is less oxidizing than Cu^{++}, it is possible that $NiCl_2$ is capable of acting similarly, since metallic Ni was found on top of the Fe_3O_4 in more than one instance. In the CE model boiler experiments, the outer surfaces of the carbon steel support, in tests where denting had been produced, were covered with metallic Cu deposits, whereas the outer surface of the supports in which denting reactions did not develop and did not have any copper deposits on them. The postulated role of reactions involving the electrochemical reduction of Cu^{++} in triggering and maintaining the denting processes seems to be further confirmed by this observation in tests where appreciable amounts of copper are present.

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* Deposited Cu or Ni metal could affect the kinetics of this reaction by providing sites of low hydrogen overpotential.

In the catalytic sense, the presense of Cu^{++} (or Ni^{++}) at the corrosion site at low concentrations would speed up the conversion of the initial corrosion product, ferrous hydroxide, to magnetite. If this should happen under conditions where the magnetite is deposited away from the steel surface because of the presence of Cl^-, then it would be non-protective and by speeding its formation Cu^{++} or Ni^{++} would accelerate the corrosion reaction. The absence of effects by already deposited Cu in the Westinghouse tests can be rationalized by assuming that deposited metal is unable to "trigger" denting.

C. Explanation of Other Observations and Future Work:

The lack of denting in the Westinghouse tests with sea water alone, using crevices between Fe and Inconel 600, is felt to be related to cathodic protection of the Inconel by Fe, and, therefore, an absence of Ni^{++} or other suitable oxidizing or catalytic ion. In tests where a soluble Ni compound is added, or in plants where hot, concentrated phosphate is known to attack Inconel in spite of the couple to carbon steel, the situation would alter and non-protective Fe_3O_4 would be formed if Cl^- were also present. Again, however, there are only triggering or catalytic functions that can be assigned to Ni^{++}, since it is present in amounts far too low to account for the massive corrosion products by a replacement reaction.

An experiment that would clarify the contribution of depolarization or the cathode by positive ions could be done by controlled electrochemical potential in the sea water experiments. If such depolarization is important, then an anodic potentiostatic test will induce denting much quicker than when it results simply from the catalytic action of low levels of Cu^{++} or Ni^{++} and it will help to explain the difference in time between laboratory and service denting.

To support the stated arguments and to extend the basic concepts of denting, more work will be needed to account for the role of the positive ions, as well as of the Cl^- ion, considering the kinetics of the catalyzed anodic reaction, the site of the deposited Fe_3O_4, the cathodic depolarization as well as the thermodynamics of the solution, i.e. the electrochemical potential - pH relationships. Such data should include a comparative evaluation of positively charged oxidizing species at different concentrations, as well as oxygen, in relation to denting in the laboratory and in service. More work is also needed to find out the effects of a combination of chemicals including hydrolyzable sea water salts, residual Ni-Fe-Cr phosphate, Cu^{++} or Ni^{++}, and Cl^{-}, so as to refine our understanding of interactions of adverse species.

As far as can be seen at this time, the CE test results are in accord with outlined mechanistic arguments, although they themselves have not emphasized the role of CuO to the same extent as this report does. These results, while not introducing any additional basic ideas, are very valuable in the practical sense, and preceded the observation of dents in plants that started without phosphate.

Concerning remedial measures, it seems that control of the environment to exclude Cl^{-}, or Cu^{++} (Ni^{++}), or to make it alkaline for a period with $Ca(OH)_2$, or to add Li-borate or boric acid are four ways of improving the situation. Cleaning of the solutions will not introduce any new factor, and could be done at any time. Additions may need further examination to ensure that no additional or new problems are introduced as side effects.

IV TUBE DAMAGE

A. U-bend Region:

A primary to secondary leak of 80 gpm in a Surry 2 steam generator led to the discovery of longitudinal intergranular stress corrosion cracking (SCC) at the apices of several tubes, originating at the primary surface. One of these was through the wall, 4" long, and had caused the observed leak. The cracking was associated with tube straining which occurred when the legs of the U-shaped region moved inwards due to TSP deformation into flow slots, or the so-called "hourglassing". The inner row of tubes in this row had the most severe straining. The cracks were longitudinal, i.e., they lay in the direction of the tube axis; there appears to be no doubt that they occurred as a result of hoop stresses that accompanied the increased "ovality" or elliptical distortion of the tubes in the U-bend region. There was a variation in the degree of ovality depending on the tube location relative to a deforming TSP flow slot. Cracked tubes were in the first row and near the centers of the distorted flow slots, i.e. in the most highly strained regions.

B. Support Plate Region:

Minor leaks were found in the support plate region also. These may be of more concern in the long run, because the size of flow slots will limit the distortion of U-bends, but denting at the support plates may continue. Also, the SCC at support plates will be very important when subsequent chemical cleaning is considered which will remove the supporting Fe_3O_4.

C. Tube Sheet Region:

There are two types of problems in the region near the top of the tube sheet of several plants. One of these is the incompletely interpreted signal that may indicate slight denting, and seen in several instances - (Cook, Tihange, Ginna, Doel). The other is the report of primary side defects, probably cracks, at Ginna[20] that have led to two leaks so far.

If there is denting in the tube sheet region, then the affected plants are beginning to undergo a problem with symptoms significantly different from plants such as Surry and Turkey Point. The latter had no denting at the tube sheets in spite of extensive dirtortion at and of the support plates. The operating history of the five plants differ completely:

TABLE V

PLANTS WITH INDICATIONS AT THE TUBE SHEET

PLANT	MONTHS PO_4	MONTHS AVT	COOLING WATER
Doel 1	3	30	Sea (with condensate polishing)
Doel 2	0	21	Sea (with condensate polishing)
Tihange 1	0	26	River
Ginna	60	29	Lake
D.C. Cook	0	27	Lake

As can be seen, cooling water is from three sources, and prior phosphate periods include 0, 3 and 60 months.

It is expected that the observations are related to the presence of sludge as well as its composition, and future details of the problem, sludge composition and secondary water analyses, when available, should be helpful in deciding whether this is a new phenomenon or just a change in the site or mechanism of rapid magnetite formation.

The suspected cracking at Ginna* needs to be considered seriously, for the following reasons:

1. There are several (5 or 6) of the reportable defects, and one has recently given rise to a minor leak.
2. There was an earlier crack, above the tube sheet, in 1976.
3. The cracks are thought to start on the primary

* Primary side cracking is not the only remaining problem in Inconel tubing, because longitudinal cracking from the secondary side in several tube sheet regions has been found in 1977 at Takahama, but more details are not yet available. This plant has been shut down since January, 1977, because of these cracks.

side. If they are stress corrosion cracks, they would indicate (a) tensile stresses due to something other than denting, since the 1976 crack was 4" above the sheet, and (b) the possibility that some of the Inconel tubes are more sensitive to SCC than has been assumed in the past, because the above mentioned tensile stresses may be quite low. Of course, since Ginna has been in operation for 7 ½ years, other plants with long operating times should be examined carefully for similar defects in order to make sure that this is not the onset of primary SCC under "normal" conditions of steam generator tubing.

D. Information Desired:

The question that now arises concerns the critical parameters for cracking, since it is desirable to be able to tell whether as yet uncracked tubes are likely to fail in the future and, if so, when. The mechanism of SCC in U-bends of Inconel 600 tubing in high temperature primary water is, unfortunately, very poorly understood, and this makes the predictions very difficult. SCC is believed to be affected by stress, strain, temperature, microstructure, electrochemical factors, heat treatment, metal composition, pH, oxygen in the environment, and other factors such as tube processing history. This complex situation helps to explain large scatter of results in laboratory tests, heat-to-heat variations in SCC resistance, and could help to rationalize the fact that some uncracked tubes in Surry 1 were more strained by ovalization than cracked tubes in Surry 2.

It is known from laboratory studies that both prior cold work and dynamic loading are not essentially required for SCC of Inconel in high temperature water, because it is well documented that plate and tube U-bends (fixed deflection) specimens can crack on long-term exposure in autoclaves. However, it remains to be shown whether, and, if so, to what degree dynamic straining and prior cold work accelerate the initiation of SCC, and the relative importance of each of these two factors in the observed service failures; (all that is definitely known today is that susceptible heats will crack if stressed or strained, sufficiently). The additional information deserves to be developed in laboratory studies as part of a broad approach to the SCC problem.

Obviously it becomes quite difficult to attempt quantitative predictions without quantitative guidelines. Therefore, it is highly desireable to obtain quantitative data regarding the factors that influence the SCC of Inconel 600 tubing, and a substantial effort is needed in this direction. Work could be spread among several well-equipped laboratories, and variables should include at least those mentioned above and should probably include alternate materials. A practical point which needs re-emphasizing is that the dented units are not the only ones for which a prediction of SCC probability is of interest, and that there will be a long term need for the type of information mentioned above.

One pertinent analysis to be made early on deals with quantitative strain and stress patterns resulting in tube U-bends as a result of bending prior to service and as a result of in-service ovalization. It is very important to obtain a quantitative number for the strain in the cracked Inconel U-bend regions. Some of the early Westinghouse data indicated about 10% strain ($\Delta\varepsilon$) during the complete flattening of a tube, which seems to be low to account for SCC at only slight ovalization, and it would be interesting to extend these calculations by means of a computer program, for instance. The other, and perhaps most critical piece of information needed is the one that would correlate the time to initiate SCC with strain or stress. Available analyses show that the service-induced hoop strain in the cracked U-tubes is quite low, in the region of 1%. Combined with the operating temperature of 575-600°F, it is apparent that SCC started much earlier than would have been predicted from laboratory data: U-bend tests (14-17% strain), normally require >5,000 hours before SCC, at 600°F.

As already mentioned, the amount of plastic strain present in cracked tubes has a strong influence on the mechanistic argument, and, therefore, the basis for making performance predictions. If the service SCC has taken place at a very low, e.g. 1%, strain, it is almost certainly necessary to introduce two additional accelerating factors: dynamic service strain and prior cold work. However, if the actual percentage strain that caused SCC is found to be much higher, then total strain could by itself account for the observed SCC in the time periods observed, and so de-emphasize the contributions of prior working and dynamic strain. Laboratory testing in this area is urgently needed. Knowledge of the processing history and chemical composition (esp. C content) of the tubes will also be helpful. Ultimately the cumulative knowledge can be used to formulate standards for SCC testing.

While more studies are carried out to obtain the desired background information, the best available guidelines are obtained from service performance. Obviously, experience from non-dented operating plants provides considerable reassurance that the combination of stress or strain, temperature, environment, etc., does not give detectable SCC within the times the plants have operated. Many thousands of tubes have performed adequately for many years; primary side cracking has been seen only in one or two cases, and in the one well-documented case*, primary water chemistry differed from current standard PWR practice in two important ways: neither an H_2 overpressure nor LiOH were present. On the more pessimistic side, however, the heat-to-heat variations in Inconel must be kept in mind, and it is not certain that experience and laboratory tests have necessarily included worst case conditions to date, or that longer operating times will not produce some SCC in general service.

Existing knowledge can already benefit future plants or the selection of replacement tubing by using the advantages of stress-relieving the U-bends to increase resistance to primary side SCC. Such heat treatments not only reduce the residual stresses in the tubes, but also can be devised to put the Inconel in a metallurgical condition that is more resistant to SCC.

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* Obrigheim

V . CRACKING OF THE TUBE SUPPORT PLATES

A few small portions of carbon steel actually became detached at Surry and Turkey Point as a result of cracks all the way through the plate thickness at some membrane regions between holes. Oxide had formed on the crack surfaces, and it was obvious that high pressure, as a result of Fe_3O_4 in numerous tube to TSP crevices, had held the loose pieces together before the wedges were cut. Embrittlement could result from hydrogen. This theory is not entirely speculative, since Westinghouse analyzed hydrogen contents as high as 2 ppm in the metal. It is possible, therefore, that local hydrogen concentrations could be even higher, for instance in highly stressed regions. Also, under certain conditions, hydrogen can react with carbon in the steel to form methane (CH_4), in which case H_2, as such, does not cause the embrittlement, but the CH_4 does. It would be interesting to find support for the H_2-related theory by verifying the absence of cracking in highly stressed areas (tension) such as flow holes where relatively less hydrogen would be expected because of lower corrosion areas. Also, an explanation of the Westinghouse observation of typically good ductility in a test piece of a TSP requires rationalization if the H_2 embrittlement theory is to hold up, i.e. could the H_2 have been lost during sample preparation?

Cracking of the partial support plates at Millstone 2 has also now been reported as a result of deformation due to denting. There are remedial steps under consideration to prevent further cracking.

VI CLEANING, INHIBITING AND OPERATING PROCEDURES:

Denting was at first thought to be confined to Surry and Turkey Point, but now it is known to affect at least a dozen plants to varying degrees. Obviously, there is an urgent need to make very rapid progress in finding cleaning methods for "slightly" dented steam generators, where the removal of the bulky magnetite will not have adverse side effects; also needed are inhibitors for preventing or stopping denting. Adequate standards for secondary water chemistry to ensure dent-free operation in the future, should also be developed.

Reported progress on inhibitors is confined to the Westinghouse work, already mentioned, with calcium hydroxide, lithium borate and boric acid.

Cleaning methods are being examined in serveral laboratories, and there are indications that some solutions are almost ready for use. Indian Point 1 and 2 are candidates for examining the effects of a cleaning solution, and much preliminary work has already been done to qualify cleaning solutions.

As far as setting chemical specifications for secondary water, this is difficult for two reasons:

1. Fixing a bulk concentration does not necessarily limit crevice conditions, and it is the crevice liquid concentration that determines whether denting will start. Increases of several orders of magnitude above the bulk water levels have been reported for Cl^-. Also, it is believed that hydrolyzable salts and cathodic depolarization or catalysis by metal ions will alter the level of Cl^- that can be tolerated before denting sets in. In support of this, the Westinghouse 10 and 0.1 fold sea water tests showed that quite high Cl^- is not bad by itself. However, in normal secondary water, with many species present in small amounts, careful Cl^- control now tentatively appears to slow the denting process. (See earlier discussion).
2. All the species and interactions that lead to denting may not yet be identified. With those that are known, little

quantitative work has been done. For instance, laboratory results so far have been in quite high bulk Cl^- solutions, in order to identify adverse species and to reproduce denting quickly. Two of the extremes in Cl^- are (a) 10 fold sea water, without denting within the test period, i.e., 150,000-200,000 ppm Cl^- in a Westinghouse test, and (b) 1 ppm Cl^- with severe denting in the presence of a mixture of Ni, Fe_3O_4, CuO, and Cu at Combustion Engineering. These data support what has been said about effects of other chemicals such as Cu^{++} together with Cl^-, and indicate a need for maintaining Cl^- levels < 1 ppm in the steam generator water, although there is no information on how much lower they need be.

In view of the lack of information to specify a Cl^- level for steam generators, any early choices will have to be made conservatively, assuming that Ni^{++} or Cu^{++} levels in the secondary system will be relatively high, as a result of corrosion of Inconel or Cu-base condenser tubes. This is not too unrealistic, since Inconel will be attacked by hot, concentrated phosphate, and Cu products are generally present throughout secondary systems, such as in sludge, and often at very high levels. More corrosion can also result from O_2 ingress during lay-up. In conjunction with conservative specifications, it will be necessary to indicate a time period during which contamination has to be removed. This decision is also complicated, but can be helped by using available data for plants with low Cl^-, using the data given in Table VI as an example.

The five examples given, where denting has occurred, cover Cu-base condensers, 0, 4, 28 and 47 months on PO_4 followed by AVT, and 81 months on PO_4 only.* They also cover cooling by brackish water, sea water and lake water. All five plants try to maintain good secondary water, yet all have some degree of denting.* Consequently, if a number for steam generator Cl^- has to be fixed on this evidence, it will have to be in the region of < .05 ppm,

* Denting yet to be confirmed positively at Robinson

with immediate action, such as maximum blowdown, power reduction and condenser isolation or demineralization as soon as .1 ppm Cl^- is exceeded. It is likely that sea water plants will not be able to meet these specifications without demineralizers. It may also be advisable to start replacing Cu-base condenser tubes with non-Cu alloys. Monitoring for dissolved Cu would also be desirable.

It is very important to be clear about the purpose of a Cl^- specification, since more Cl^- may be tolerated in a clean steam generator than in one with active crevice corrosion.

It is evident that, before there can be a meaningful attempt at setting specifications for impurities in secondary water, we need to analyze and obtain much more information than has been available for this report, including details of field observations, as well as laboratory studies of essential and basic parameters, i.e. electrochemical potential (e.g. Cu^{++}, Fe^{++}, Ni^{++} and O_2), pH (H^+), and aggressive anions (such as Cl^-). Before that is done, efforts by the utilities to maintain Cl^- below .05 ppm should be encouraged.

TABLE VI

COMPARISON OF CHLORIDE LEVELS IN SOME OPERATING PLANTS

PLANT	MONTHS ON PO_4	Cl^- ppm TOLERATED	ACHIEVEMENT	RESULTS
Maine Yankee	0	.05 ppm	60 days > 1 ppm. Few excursions about 30 ppm	Minor denting in 1975-1977 period
Ringhals 2	4	< .1 ppm	No dents 1975. Since then, 5 excursions > .1 ppm 19 days out of spec. All < 1 ppm.	Moderate denting in 1975-1977
Point Beach 1 and 2	47,28	< .15 ppm	Condensers leaked	Moderate dents
Robinson*	All	Not available but lake water reported to be < 1 ppm	Expected to be very low, in view of cooling water composition	Minor dents, or none
Japanese Plants		Reported meticulous care to maintain "clean" secondary systems.		No denting

* Reference 1 warns that phosphate could be directly involved in forming non-protective oxide on steels in boilers.

VII SUMMARY

1. Some degree of denting due to non-protective magnetite formation has now been found in 14 PWR plants with recirculating steam generators in the U.S. It has occurred with and without prior phosphate exposure in operating steam generators and in laboratory tests, and two plants still on phosphate have been affected, but it is suspected that phosphate additions may have been interrupted at times.*
2. Both the incidence and degree of denting appear to be related to the quality of the secondary water, i.e. a combination of condenser performance and plant procedures that are followed in dealing with impurities.
3. Acid chloride is needed for denting to occur. A review of recent laboratory data confirms the earlier observations of Potter and Mann[3] that Cl^- alone is not sufficient, and it is believed that its harmful level will vary according to the presence of other ions in solution. Oxidizing species, combined with chloride and crevices can result in local changes that promote the rapid Fe_3O_4 reaction. The oxidizing species could be relatively high levels of Cu^{++} or Ni^{++} or oxygen, for example. Active metal ions such as Cu^{++} or Ni^{++} may also catalyze the anodic formation of magnetite, even when present at low concentrations. The active ingredients can result from feedwater heater corrosion, or poor condenser performance and condenser tube corrosion. Consequently, all of the following are considered as adverse and provision for monitoring them, where feasible, would be advantageous: Cl^- inleakage, condenser tube corrosion products, Inconel corrosion products from reaction with impurities or prior phosphate treatment, other hydrolyzable chlorides that produce a low pH environment, feedwater heater corrosion.

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* Direct involvement of PO_4 in rendering Fe_3O_4 non-protective has not been ruled out. (Reference 1).

4. Ions in solution are considered more harmful than deposited metals such as Cu and Ni, although the latter could contribute to the kinetics of denting by means of catalytic action and of providing low hydrogen overpotential sites; cathodic hydrogen evolution from the decomposition of water accompanies the run-away magnetite growth once the reaction has been "triggered".

5. There is an absence of information needed to set meaningful specifications for secondary water purity.* This is due in part to the incomplete availability and analysis of data from operating plants, but also involves the fact that local concentrations and interaction of ions in solution diminish the value of, say, monitoring bulk conductivity or Cl^- level. Conservative levels of Cl^- in steam generators, assuming other factors to be also adverse, appear to be 0.1 or even 0.05 ppm to avoid denting, and may be even lower for already denting units. Sea water cooled plants may need demineralizers to achieve the desired levels if they are so low.

6. Inhibitors such as lithium borate, H_3BO_3, $Ca(OH)_2$ hold promise for arresting denting, as does operation that ensures very low levels of contamination.

7. Alternate condenser tubing and feedwater heater materials should be considered in order to lower inleakage and possible Cu ion accumulation.

8. There may be a new problem or merely a change in location of denting sites, based on observations of abnormal EC signals at the top of tube sheets. At this time this has been seen in several steam generators, but damage is very slight and incompletely inspected and reported.

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* Where not otherwise stated, reference is made in this report to Cl^- in the steam generator itself, i.e. blowdown. (Even low levels of contaminants in the condensate means massive inleakage, because the condensate is so voluminous).

9. Stress corrosion cracking can occur in Inconel tubing from the primary side if stress and strain are very high, as at Surry and Turkey Point. Stress corrosion cracks within the tube sheet or above it have also been found at Ginna, with one recent leak. An earlier leak occurred a year ago. The leaks were very small. This may be associated with the phenomenon in "8" above, and may be a warning that some Inconel 600 tubes could be quite susceptible to primary side cracking, because there is as yet no indication of high stress at this plant. The observations may also indicate that stresses from sources other than denting can result in primary side cracking, and points to a need to develop information relating the condition of Inconel 600 to stress corrosion cracking; stress levels, temperature and environmental conditions need to be defined so as to have a basis for licensing considerations in cases where in-service leaks occur. In view of the fact that Ginna has been in operation for 7 ½ years, there may also have been a cumulative time effect in the formation of the defects, and other plants approaching this age should be examined carefully for similar defects.

10. In addition to studies of denting - its origin and cure, it is felt to be very important that chemical cleaning developments for steam generators be actively pursued. These should be worked out so as to maximize scale and sludge removal without harmful side effects. Also, careful attention should be given to the matter of when chemical cleaning is advisable, and when damage is so severe that cleaning would be risky. A reliable chemical cleaning procedure may eventually become part of a preventative maintenance program during regular outages.

VIII ACKNOWLEDGEMENTS

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