

## **B.7 "Corrosion of Steam Generator Tubes,"** by Roger W. Staehle

### **Introduction**

The objective of this background paper is to describe the corrosion of tubing materials used in PWR steam generators of LWRs. This tubing includes Alloys 600MA, 600TT, 690TT and 800. The corrosion behavior of these materials has been discussed comprehensively by Staehle and Gorman.<sup>1</sup> This present report emphasizes mainly the initiation stage of SCC since SG tubes are relatively thin compared to thicker sections in pipes and various instrument and control rod housings. Some information on SCC propagation is included. As used in this paper, the term failure means degradation and/or cracking to varying degrees (depending on the context); sometimes such degradation would require tube plugging or repair and other times, failure relates to crack initiation.

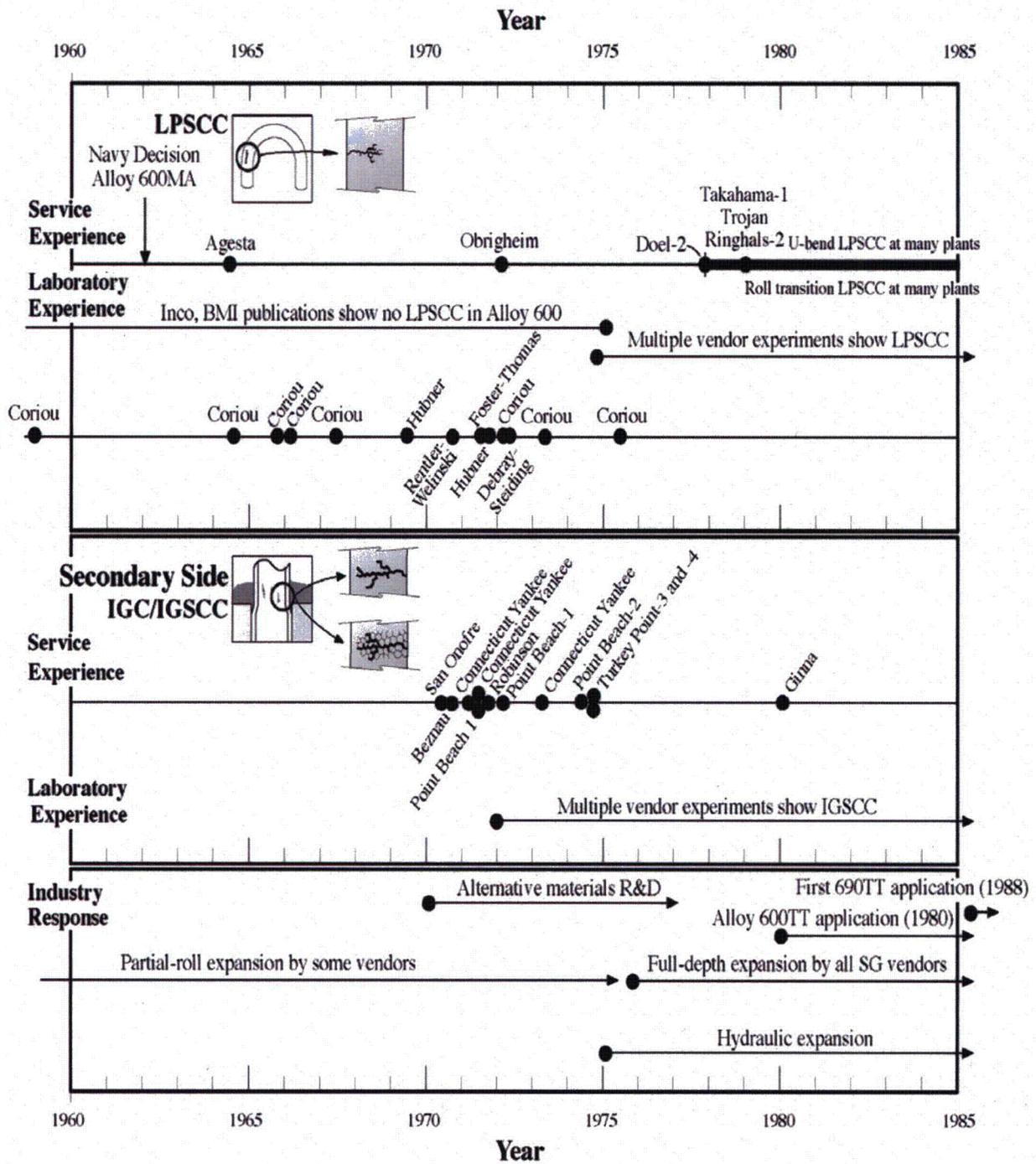
This discussion considers the development and application of Alloy 600MA, Alloy 600TT, Alloy 690TT and Alloy 800, together with the modes of corrosion they sustain and some of the principal dependencies of these modes of corrosion.

The terminology of MA (mill-annealed) and TT (thermal treatment) is used in this discussion. MA for Alloy 600 is heat treated at about 1000°C and for Alloy 690 at about 1070°C. TT for Alloy 600 is heat treated at 700°C for 15 hours and for Alloy 690 at 716°C for 10 hours. A slight variation for MA is given by LTMA (low temperature mill-annealed) and HTMA (high temperature mill-annealed). LTMA is heat treated at 985°C and HTMA at 1010°C.

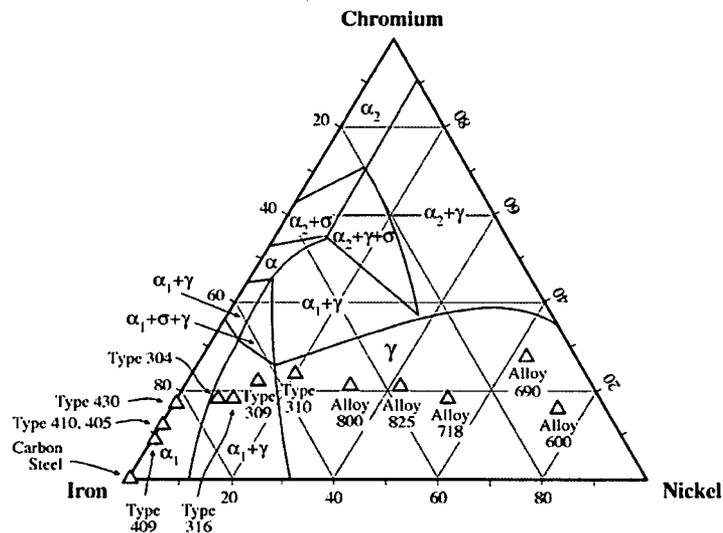
The earliest tubing used in steam generators was the Type 304 stainless steel in the Shippingport plant<sup>2</sup> and noted in Scharfstein et al.<sup>3,4</sup> However, even with the horizontal steam generators used in this application, chlorides and caustic were concentrated at the tube supports and tubesheets thereby producing SCC. In 1962 the Navy program decided to use Alloy 600MA in steam generators, and the subsequent evolution of the use of alloys in LWRs is shown in Figure B.7.1. The Russian designed VVERs followed a different path, continuing to use horizontal austenitic stainless steel tubes terminating at vertical cylindrical collectors. On the whole, these have been reliable in service.

The alloys used for steam generator tubing are nominally single phase with a face centered cubic structure, usually called an "austenitic structure," as shown in the ternary diagram of Figure B.7.2.<sup>5</sup> Chemical compositions of the alloys for SG tubing and for tube supports are given in Table B.7.1.

The choice of the high nickel alloys for replacing the stainless steels for SG tubing was based essentially on the work of Copson and Cheng,<sup>6</sup> who had studied the effect of nickel on the SCC of Fe-Cr-Ni alloys in boiling MgCl<sub>2</sub> solutions as shown in Figure B.7.3a. This work showed that the alloys with nickel concentration exceeding about 40w/o would resist SCC in the concentrated MgCl<sub>2</sub> solutions. By implication, and assuming that the boiling MgCl<sub>2</sub> solutions represented characteristically aggressive solutions generated from seawater or estuarine water ingress at leaking condensers, these results suggested that the high nickel alloys would resist a broad range of stress corrosion cracking. Figure B.7.3b from Berge and Donati<sup>7</sup> shows results from SCC testing of Alloy 600MA in a boric acid solution containing chloride at 100°C; and in contrast, found extensive transgranular SCC in Alloy 600.



**Fig. B.7.1** Service and laboratory experience with LPSCC and IGSCC vs. time. Industry response to these experiences vs. time. From Staehle and Gorman.<sup>1</sup> © NACE International 2003/2004.



**Fig. B.7.2** Alloys of interest to steam generators superimposed on Fe-Cr-Ni ternary diagram for 400°C. Fe-Cr-Ni diagram from Pugh and Nisbet.<sup>5</sup> Reprinted with permission from TMS.

**Table B.7.1** Composition of Alloys Used in Tubing and Tube Supports (maximum w/o, except where noted)

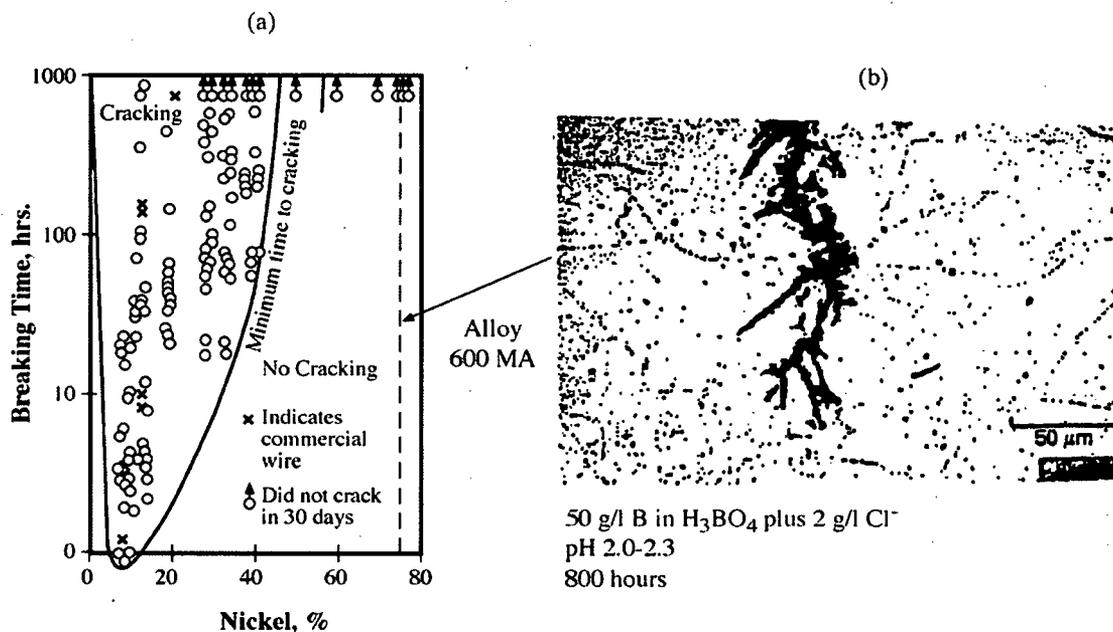
Elem.	Type 304 <sup>[A]</sup>	Type 316 <sup>[A]</sup>	Alloy 600 EPRI Guidelines <sup>[B]</sup>	Alloy 690 EPRI Guidelines <sup>[C]</sup>	Alloy 800 Nuclear Grade <sup>[D]</sup>	Carbon Steel ASTM A285 Gr C <sup>[A]</sup>	Type 405 ASME SA479 <sup>[A]</sup>	Type 409 <sup>[A]</sup>	Type 410 ASME SA479 <sup>[A]</sup>
C	0.08	0.08	0.025-0.05	0.015-0.025	0.03	0.28	0.15	0.08	0.15
Mn	2.00	2.00	1.00 max.	0.50	0.4-1.0	0.90	1.00	1.00	1.00
P	0.045	0.045	0.015	0.015	0.020	0.035	0.040	0.045	0.040
S	0.03	0.03	0.010 max.	0.003	0.015	0.035	0.030	0.045	0.030
Si	1.00	1.00	0.50 max.	0.50	0.3-0.7	-	0.50	1.00	1.00
Cr	18-20	16-18	15.0-17.0	28.5-31.0	20-23	-	11.5-13.0	10.5-11.75	11.5-13.5
Ni	8.0-10.5	10-14	>72	Bal. (>58)	32-35	-	-	0.50	-
Mo	-	2.0-3.0	-	0.2	-	-	-	-	-
Fe	Bal.	Bal.	6.0-10.0	9.0-11.0	Bal.	-	Bal.	Bal.	Bal.
Cu	-	-	0.50 max.	0.10	0.75	-	-	-	-
Co	-	-	0.015 ave.	0.014	0.10	-	-	-	-
Al	-	-	-	0.40	0.15-0.45	-	-	-	-
Ti	-	-	-	0.40	0.60	-	-	6xC-0.75	-
Other	-	-	-	N = 0.050 B = 0.005 Nb = 0.1	Ti/C ≥ 12 Ti/(C+N) ≥ 8 N ≥ 0.03	-	-	-	-

[A] From ASM Handbook.<sup>8</sup>

[B] From EPRI.<sup>9</sup>

[C] From Gorman.<sup>10</sup>

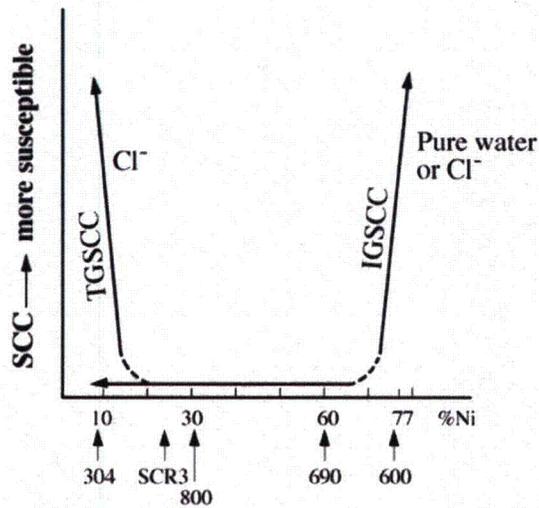
[D] From Stellwag et al.<sup>11</sup>



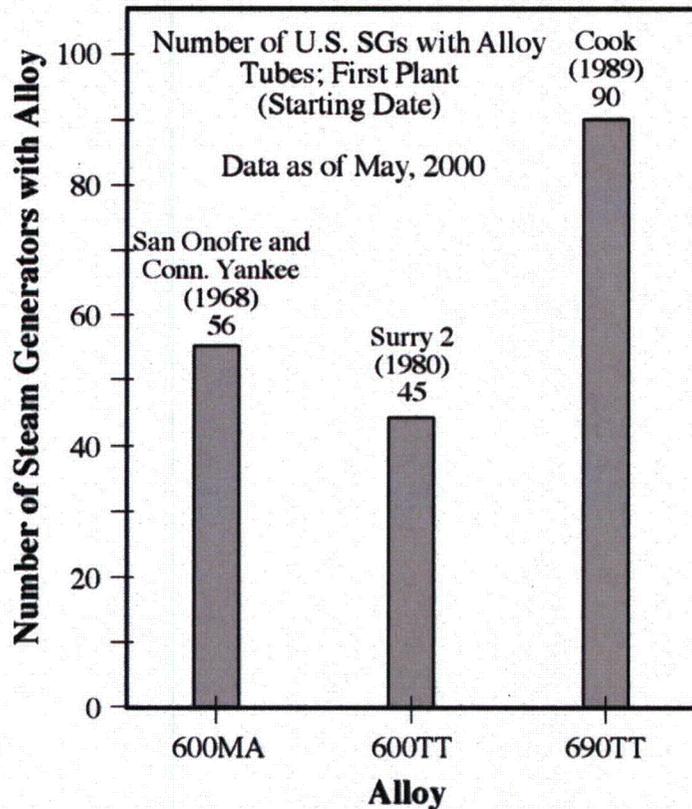
**Fig. B.7.3** (a) Breaking time vs. Ni (in wt.%) for Fe-20Cr-Ni alloys exposed to 42% boiling MgCl<sub>2</sub>. pH of solution is about 4.1. From Copson and Cheng. (b) Photomicrograph of Alloy 600MA exposed at 100°C in a solution containing 50 g/l boron as boric acid and 2 g/l Cl<sup>-</sup>. pH of solution is 2.0 to 2.3. U-bend specimen examined after 800h. From Berge and Donati<sup>7</sup> © 1981 American Nuclear Society.

At about the same time as Copson and Cheng had published the work in Figure B.7.3a, Coriou et al. published their work on the SCC of high nickel alloys which were exposed to 100°C pure water.<sup>12</sup> This 1959 paper, together with subsequent ones, showed conclusively that Alloy 600 would sustain SCC in pure deaerated water. Coriou et al.<sup>13</sup> then published a schematic view shown in Figure B.7.4 indicating that the SCC in pure deaerated water was most aggressive in high nickel alloys while the SCC in chloride solutions was most aggressive in low nickel alloys following Figure B.7.3 from Copson and Cheng. This figure indicated that an optimum material would be in the mid-range of nickel concentration. This observation was the basis for choosing Alloy 800 for some SG tubing as well as indicating that the Alloy 690 composition, to be developed later, would be attractive.

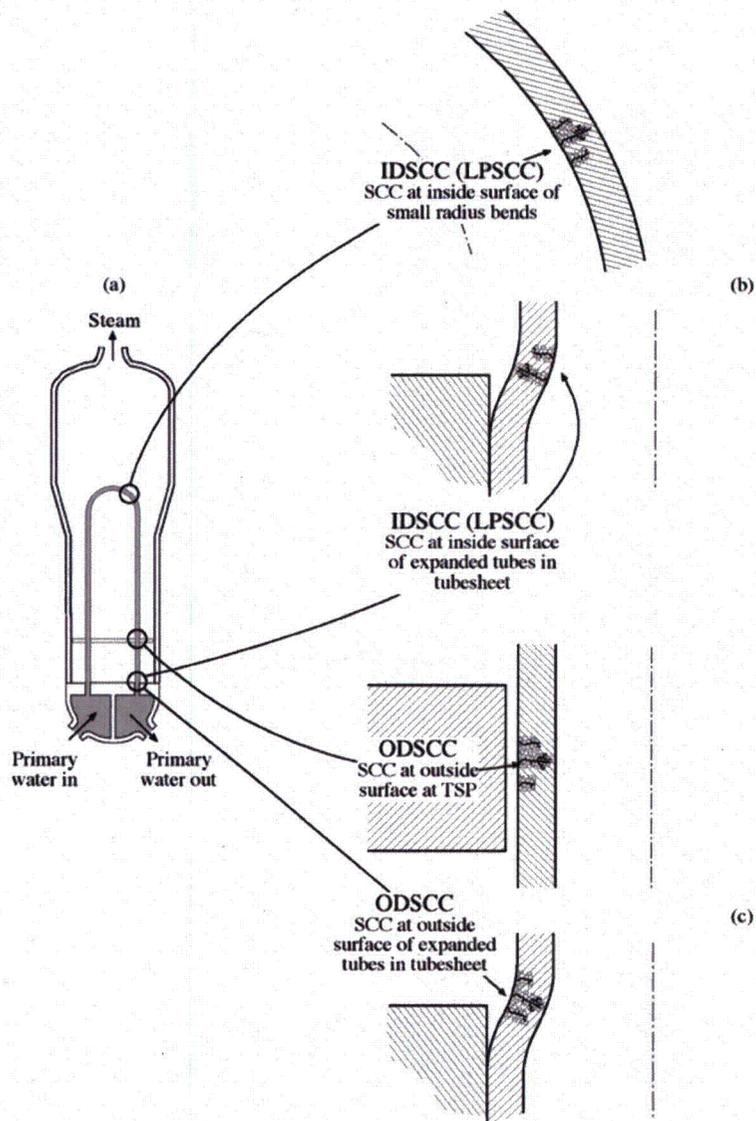
In summary, the chronology of corrosion of tubing in PWR steam generators has been dominated by extensive SCC on both the inside and outside of the Alloy 600 tubes. The application of improved alloys has responded to this corrosion first with Alloy 600TT and then with Alloy 690TT as shown in Figure B.7.5. Today, Alloy 690TT is increasingly used for replacement steam generators because of its improved corrosion resistance; although it should be noted, as shown in Section 4.0, that Alloy 690TT is not immune to SCC. In addition, Alloy 800 has given excellent service, as predicted by Coriou et al. in Figure B.7.4, in operating SGs.



**Fig. B.7.4** Schematic view of SCC intensity vs. Ni concentration for Fe-Cr-Ni alloys in high temperature water for pure deaerated water and chloride-containing water. Important commercial alloys noted. From Coriou et al.<sup>13</sup> © NACE International 1969.



**Fig. B.7.5** Number of U.S. steam generators with various alloy tubing as of May 2000. First plant to use the alloy and start dates noted. Private communication from P. Scott, Framatome and Al McIlree, EPRI. Note that Alloy 800 continues to exhibit excellent performance in international applications.



**Fig. B.7.6** Schematic view of principal location of SCC damage. SCC from the primary side is mostly stress-related and from the secondary side is mostly chemistry related.

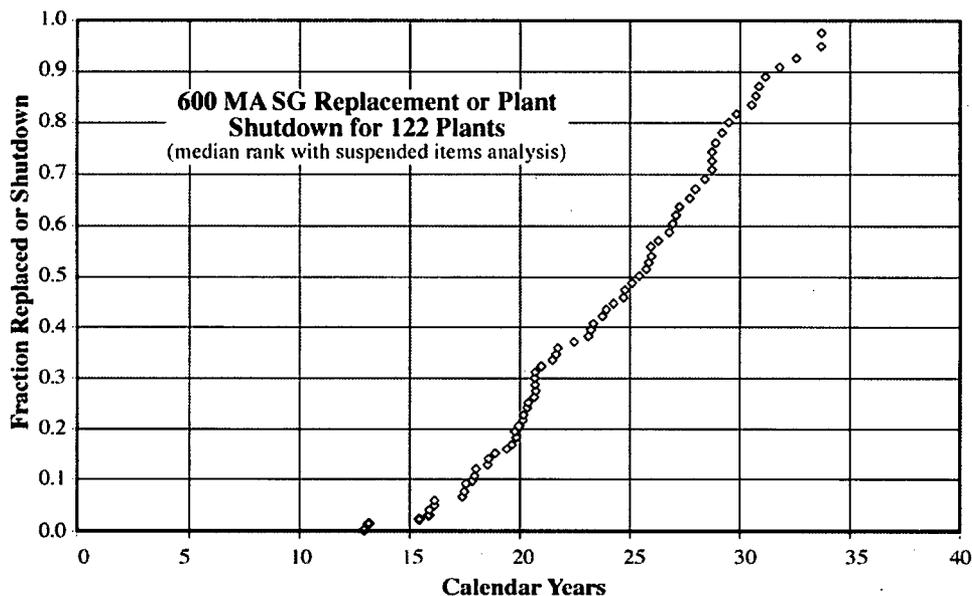
Corrosion of Alloy 600 steam generator tubes has occurred both on the inside surface (IDSCC) as well as the outside surface (ODSCC) as shown in Figure B.7.6. On the inside primary surfaces, SCC has occurred mainly at locations of relatively high stresses and high temperatures. These high stresses occur at the tubesheet where the tubes are expanded and at the U-bends, especially the inner U-bends where the radii of curvature are the smallest. SCC on the primary side also occurred during the slow straining associated with "denting." On the outside surfaces, SCC has occurred mainly on surfaces inside heat transfer crevices both at the top of the tubesheet and at tube supports. This corrosion has occurred again mainly at the hottest locations along the tubes; although the stresses at these locations, except at the top of the tubesheet, were nominal being associated with pressure forces and residual stresses due to

fabrication of the tubes. SCC on the outside surfaces has also occurred in free span locations often associated with scratches.

Much of the corrosion that has occurred in the Alloy 600 tubing of SGs has resulted from erroneous assumptions:

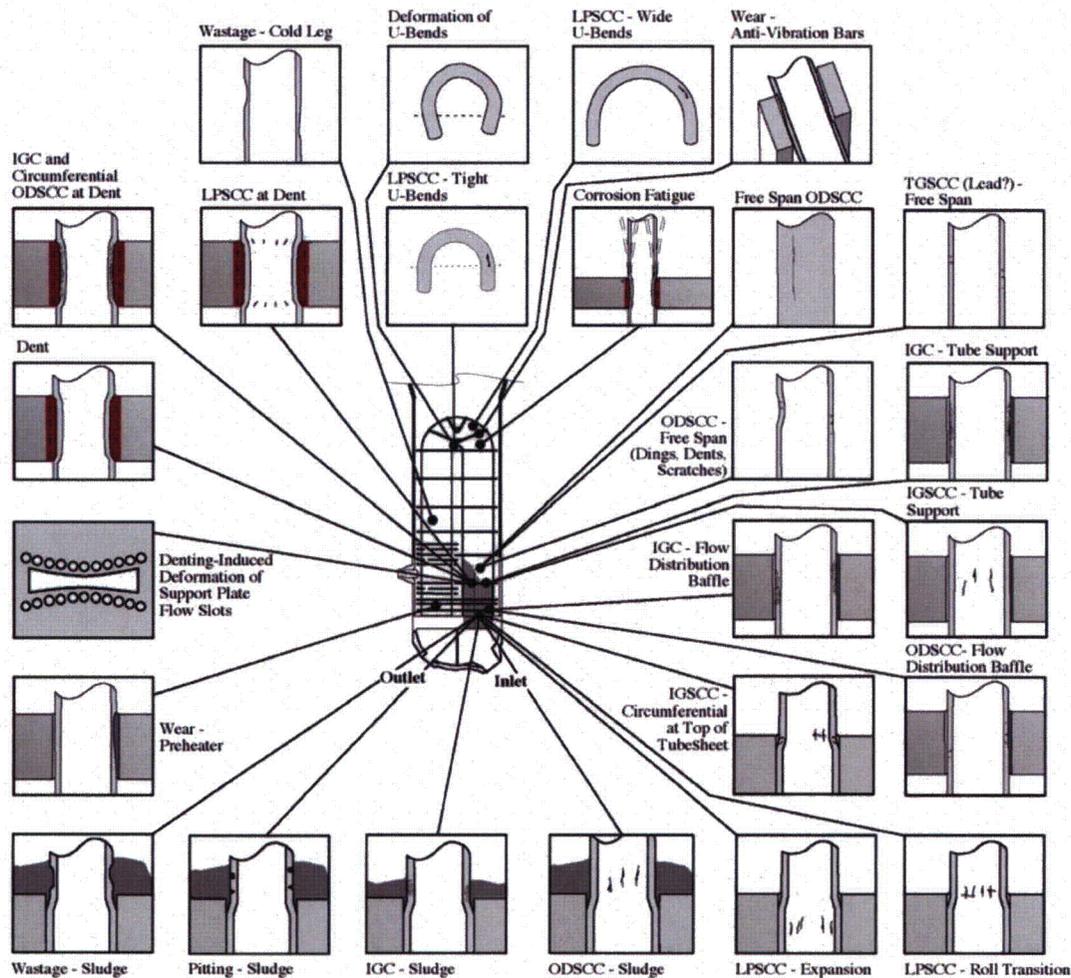
- Assumption that Copson and Cheng's data, Figure B.7.3, were correct as were the implications for adequate performance in other environments.
- Assumption that the Coriou et al. data were not applicable and erroneous.
- Assumption that water chemistry that worked in fossil systems would work on the secondary side of PWR SGs.
- Assumption that significant fouling and hence corrosive concentrations would not occur in drilled hole heat transfer crevices.
- Assumption that residual stresses in expanded regions and in straight tubes were not sufficient to produce SCC.

Figure B.7.7 shows the chronology for the replacement of SGs. These replacements resulted from corrosion degradation.



**Fig. B.7.7** Fraction of replaced or shutdown steam generators vs. calendar years for Alloy 600MA plants in the world. From Dow, Jr.<sup>14</sup> Used by Permission of EPRI.

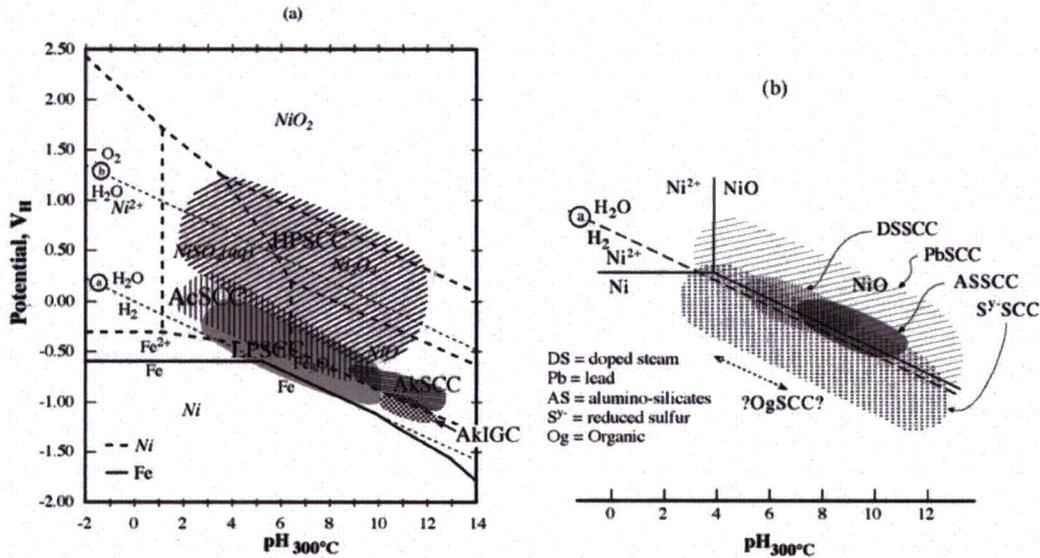
Failures involving multiple modes of corrosion and multiple locations occurred with the combination of Alloy 600MA as it was exposed on both primary and secondary sides. The multiple mode-location cases of degradation with Alloy 600MA and with drilled holes on the secondary side, are summarized in Figure B.7.8. Here, there are 25 mode-location cases of degradation associated with the use of Alloy 600MA.



**Fig. B.7.8** Array of modes of degradation at various locations (mode-location cases) that have occurred in recirculating steam generators using Alloy 600MA at drilled hole tube supports. From Staehle and Gorman.<sup>1</sup> © NACE International 2003/2004.

As these failures, which are shown in Figure B.7.8, evolved, extensive corrosion studies were undertaken both in the laboratory and of failed tubes. These experiments included studies of SCC on the primary side, where there were no crevices, and the secondary side, where there were extensive heat transfer crevices. SCC was identified in regions that were not so surprising based on the past history of SCC in steels and stainless steels. Figure B.7.9 shows the locations of the occurrence of SCC in the framework of the electrochemical variables of pH and potential. The occurrence of such SCC in the acidic, alkaline, low potential and high potential regions corresponds generally with regions where protective films are transiently unstable when broken. The bases for the diagram shown in Figure B.7.9a are described by Staehle and Gorman.<sup>1</sup> In addition to the diagram in Figure B.7.9a that shows the “primary” submodes of SCC, Figure B.7.9b shows the general locations of other submodes of SCC. Again, this diagram has been extensively described by Staehle and co-workers. Also, a similar diagram has been published by Combrade et al.<sup>15,16,17</sup> The term, “submode,” refers to the corrosion mode of SCC, but differentiates occurrences of unique dependencies on the primary variable of

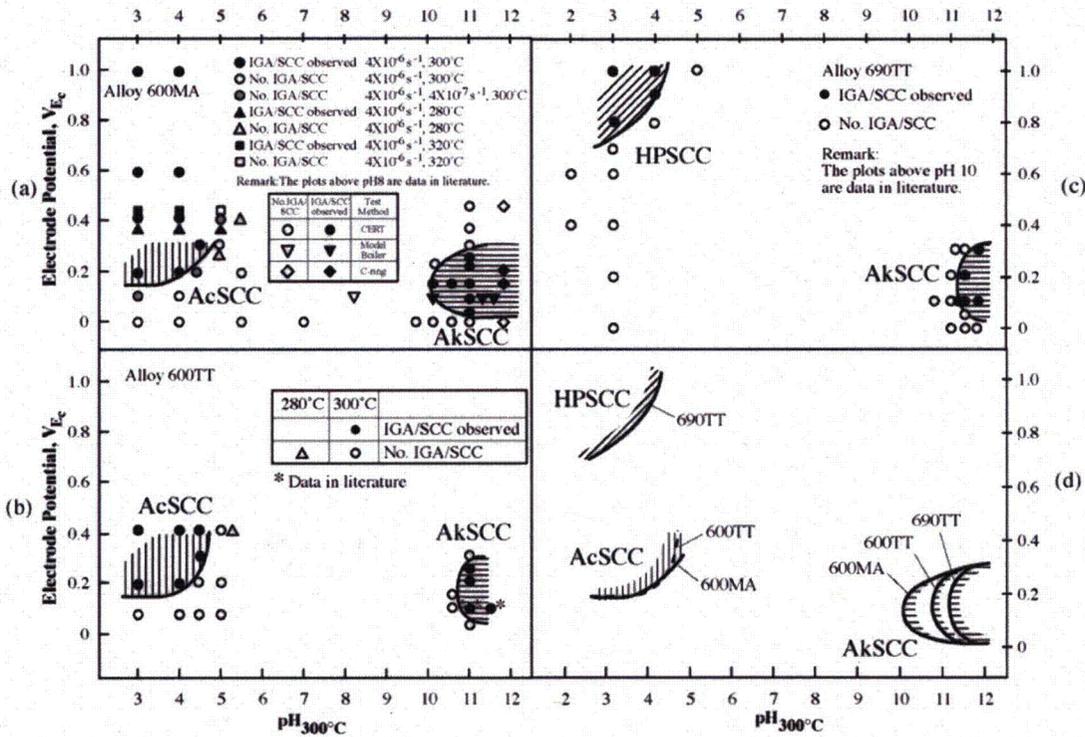
pH, potential, species, alloy composition, alloy structure, temperature, and stress (e.g. each submode consists of a different set of dependencies).



**Fig. B.7.9** (a) Major submodes of SCC plotted with respect to coordinates of potential and pH for significant SCC occurrences at 300°C. Extent of the submodes based on experience from laboratories and reasonable interpolations and extrapolations. Submodes applicable to Alloy 600MA in the range of 300 to 350°C. (b) Minor submodes of SCC for Alloy 600MA plotted with respect mainly to the NiO/Ni half cell equilibrium at 300°C. From Staehle and Gorman.<sup>1</sup> © NACE International 2003/2004.

The mode diagram of Figure B.7.9 has been verified also by systematic experimental and review work of Ohsaki et al.<sup>18</sup> and by Tsujikawa and Yashima<sup>19</sup> as shown in Figure B.7.10; and they have extended the framework to Alloys 600TT and 690TT. These alloys are discussed in Sections 3.0 and 4.0, respectively. It should be noted that in some cases the regions of SCC in Figure B.7.10 are not complete, as shown by Staehle and Gorman.<sup>1</sup>

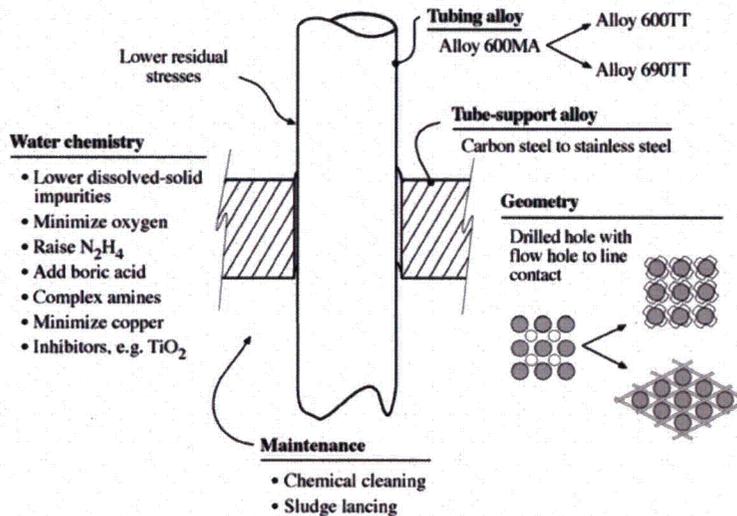
This early evolution of SCC associated with Alloy 600 has been eventually mitigated as shown in Figures B.7.11 and 12 where the various mitigations in alloy, water chemistry, and design are summarized: Alloy 600MA was replaced by Alloys 600TT and 690TT; the water became more pure and certain inimical species, such as copper, were eliminated; the drilled hole tube support was eliminated in favor of the line contacts; and residual fabrication stresses were lowered.



**Fig. B.7.10** IGA/SCC tests results in the range of 180 to 320°C range as a function of electrode potential and pH taken at 300°C for (a) Alloy 600MA, (b) Alloy 600TT, (c) Alloy 690TT. From Ohsaki et al.<sup>18</sup> (d) Comparison of IGA susceptibility among Alloy 600MA, Alloy 600TT, and Alloy 690TT in the range of 280 to 320°C as a function of electrode potential and pH taken at 300°C. From Tsujikawa and Yashima.<sup>19</sup> Permission granted by Canadian Nuclear Society.

### Alloy 600MA - Introduction

Alloy 600MA was the alloy used widely for tubing in SGs of PWRs from 1962 through the mid-1980s in France, Japan, Spain, Sweden and the US. The corrosion that occurred with the use of Alloy 600MA resulted in the replacement of the steam generators as shown in Figure B.7.7. Replaced SGs have primarily been tubed with Alloys 600TT or 690TT with the latter being preferred as indicated in Figure B.7.5. Alloys 600TT and 690TT as well as Alloy 800 have given excellent service as discussed below.

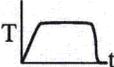


**Fig. B.7.11** Schematic view of changes in maintenance, materials, designs, and water in order to minimize the corrosion of the tubing. From Staehle and Gorman.<sup>1</sup> © NACE International 2003/2004.

During the Alloy 600MA period, corrosion was dominated by two general patterns, mainly of SCC. One was SCC from the ID of the tubes, which was exposed to high purity primary water containing the standard chemical additions of hydrogen, boric acid and lithium hydroxide. The other was SCC and some corrosion from the OD, which was associated mainly with impurity chemicals that were concentrated in the superheated crevices of tube supports and at the top of tubesheets. Figure B.7.6 shows these essential locations, which are discussed below.

The overall chronology of modes of corrosion of Alloy 600 has been described in two different figures as shown in Figure B.7.13. These figures both show the same trends. An early mode of failure was general corrosion associated with phosphate water chemistry in those plants that adopted this secondary water treatment. Following this, IGSCC occurred, which was mainly due to concentrations of alkaline impurities. Next was denting involving the corrosion products from corroding carbon steel tube supports pressing on the tubes to constrict the diameter. Next was an increase in IGSCC on the primary side followed by more IGSCC on the secondary side. These patterns involve mainly the occurrence of corrosion in Alloy 600MA.

Essentially, the evolution of corrosion concerning Alloy 600MA involved mitigating one mode only to find the intensification of another; such was the sensitivity of this alloy to corrosion.

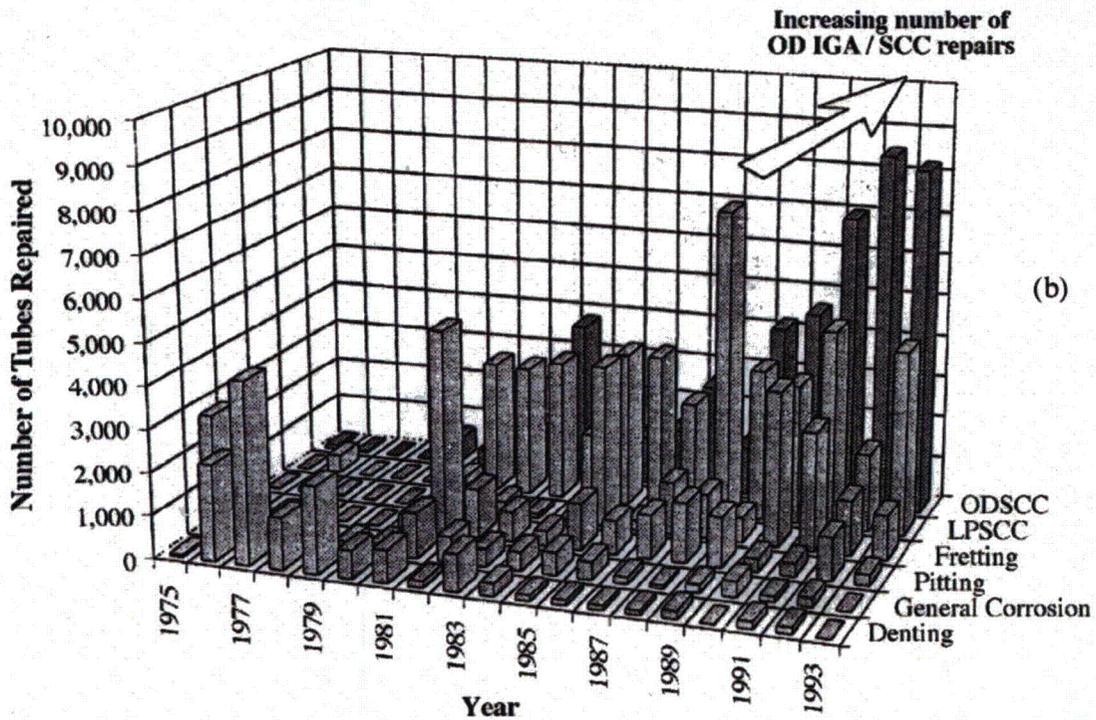
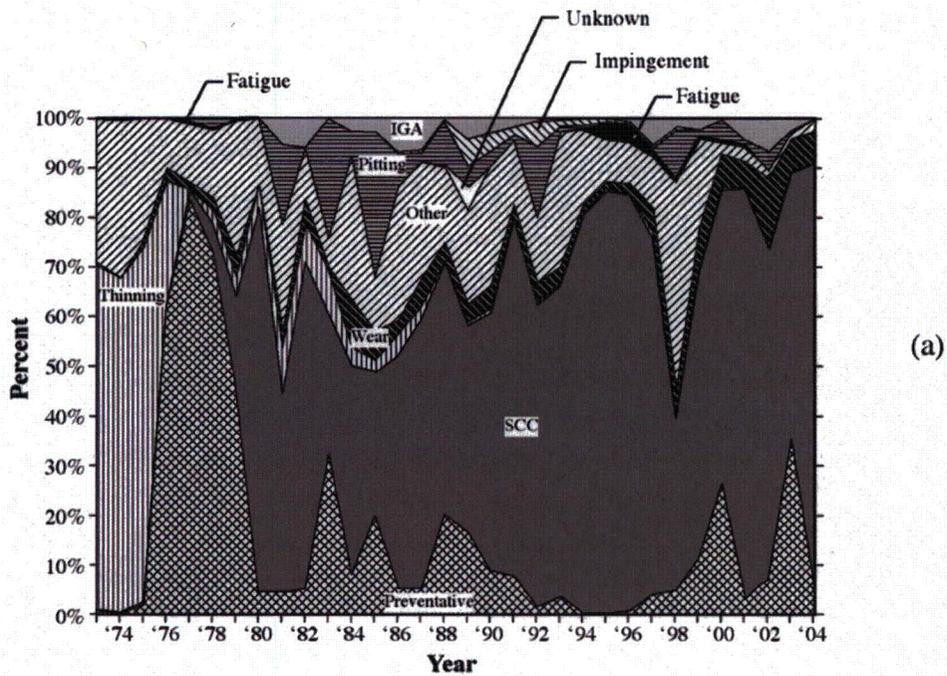
	Model D3, Virgil Summer	Model F
<b>Tube material</b>	Inconel 600MA 	Inconel 600TT or 690TT 
<b>Heat treatment</b>	Low temperature mill anneal (LTMA) 	Thermal treatment (TT) 
<b>Tube support hole</b>	Drilled hole, circular 	Quatrefoil 
<b>Tube support material</b>	Carbon steel 	Stainless steel 
<b>Flow holes</b>	Yes 	None 
<b>U-bend stress relief</b>	None 	Yes 
<b>Tube sheet expansion</b>	Mechanical expansion 	Hydraulic expansion 
<b>Blow down</b>	Original design 	Better location, increased capacity 
<b>Secondary Side Access</b>	Original design 	Improved 

**Fig. B.7.12** Comparison of Models D3 and F from Westinghouse design plants where changes are intended to minimize corrosion of the tubing. From Staehle and Gorman.<sup>1</sup> © NACE International 2003/2004.

### SCC of Alloy 600MA on the ID

SCC on the ID (primary) surfaces of SG tubes is mainly associated with Alloy 600MA, and such SCC has contributed substantially to the failure and widespread replacement of steam generators shown in Figure B.7.7. This section summarizes the main dependencies of SCC on the ID of Alloy 600MA tubes.

Since the SCC on the inside of Alloy 600MA tubes has been associated with the primary side or inside of the tubes, it was initially called "PWSCC" or "Primary Water SCC." This is also interpreted by some as "Pure Water SCC." Both terms however are misleading as they imply that this SCC can occur only on the primary side. A better terminology is "Low Potential SCC (LPSCC)," since this SCC is principally characterized by its occurrence at low electrochemical potentials, as shown in Figure B.7.9, just as some SCC occurs exclusively in the alkaline region and is called AkSCC. Incidentally, as a supporting note here, efforts to reproduce the early work of Coriou failed to identify this SCC, most likely due to the lack of sufficient deaeration of the tests.



**Fig. B.7.13** Chronology of modes of corrosion vs. time mainly for Alloy 600 in drilled hole tube supports. (a) Two dimensional. From Dow, Jr. (b) Three dimensional. From Varrin, Jr.<sup>20</sup> Used by Permission of EPRI.

Principal characteristics of LPSCC in Alloy 600MA are the following according to the seven primary variables that affect aqueous corrosion:

### 1. pH

LPSCC is generally independent of pH over a range from about pH 3 to pH 9 as summarized by Staehle and Gorman.<sup>1</sup>

### 2. Potential

A central feature of LPSCC has been its confinement to low potentials in the general range of the  $H_2O/H_2$  and  $NiO/Ni$  equilibria. There seems to be a tendency for LPSCC to be maximum, both in initiation and propagation, at the  $NiO/Ni$  equilibrium, as shown in Figure B.7.14.<sup>15,21,22</sup> In each figure the location of the  $NiO/Ni$  equilibrium potential is noted; this is an invariant and thermodynamically defined line, not depending on concentration of species in solution. Figure 14a is based on testing of initially smooth specimens; and Figure 14b is based on initially precracked specimens. Thus, the former relates to conditions of initiation and the latter relates to propagation.

### 3. Species

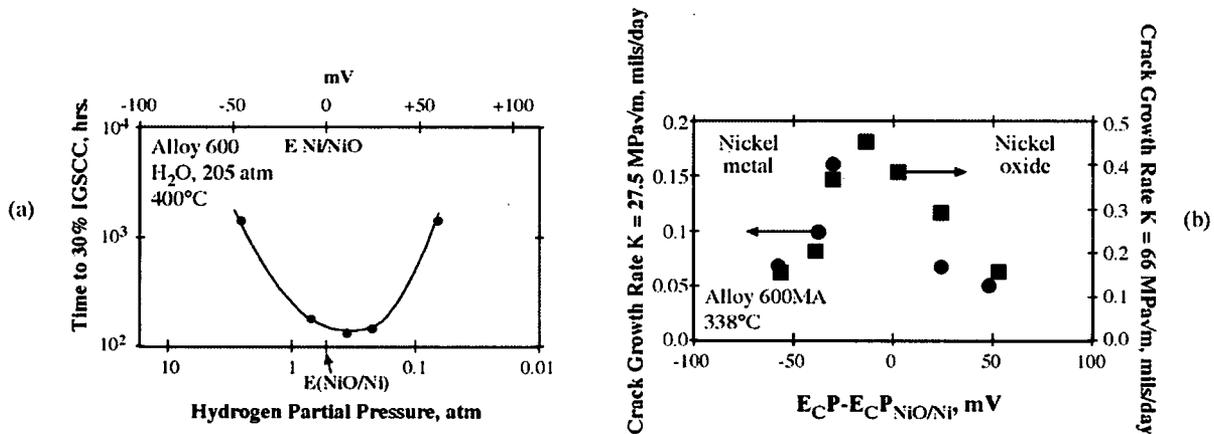
LPSCC has been investigated with respect to concentrations of boric acid and lithium hydroxide as summarized by Staehle and Gorman.<sup>1</sup> Effects of these species are not significant. However, there has been little investigation of effects of chloride, sulfate, or other species over significant ranges of concentration; this lack of breadth impedes connecting LPSCC to domains of chemistry that might be important to the secondary side.

### 4. Alloy composition

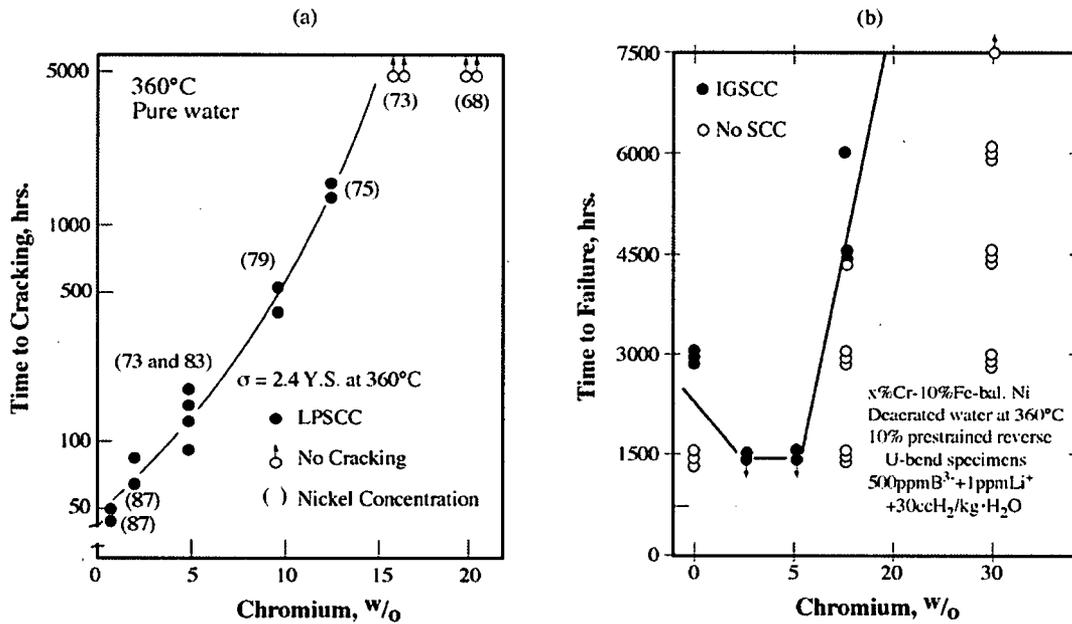
Another defining characteristic of LPSCC is its dependence upon alloy composition. With respect to the concentration of chromium, the data from two different investigations in Figure B.7.15<sup>23,24</sup> show that increasing chromium decreases sensitivity to LPSCC. It is noteworthy that Fe-Ni alloys sustain rapid LPSCC and that LPSCC is negligible above 20% Cr, which is relevant to the compositions of Alloy 690 with a Cr content around 30% and Alloy 800.

### 5. Alloy structure

LPSCC is generally influenced by the distribution of carbides. As carbides accumulate at grain boundaries, LPSCC is minimized. Figure B.7.16 shows this effect from work by Norring et al.<sup>25</sup> and Cattant et al.<sup>26</sup> A further important result was published by Blanchet et al.<sup>32</sup> where they showed that sensitization greatly reduced the sensitivity to LPSCC as shown in Table B.7.2.



**Fig. B.7.14** (a) Time to 30% IGSCC vs. hydrogen pressure and potential reference to NiO/Ni equilibrium. Experiments at 400°C and 205 atm pressure of steam. Original data from Economy et al.<sup>21</sup> Dependencies recalculated by Scott and Combrade.<sup>15</sup> © 1997 American Nuclear Society. (b) Crack growth rate at two stress intensities vs. potential ( $E_C P$ =electrochemical potential) relative to the NiO/Ni equilibrium potential for Alloy 600MA at 338°C. From Morton et al.<sup>22</sup> © NACE International 1987.



**Fig. B.7.15** (a) Time-to-cracking vs. concentration of Cr for Ni-Cr-Fe alloys exposed in pure water at 2.4 Y.S. at 360°C. From Yonezawa and Onimura.<sup>23</sup> Courtesy of ISIJ. (b) Time-to-failure as concentration of Cr for Fe-Cr-Ni alloys with 10w/o Fe. From Nagano and Kajimura.<sup>24</sup> © NACE International 1995.

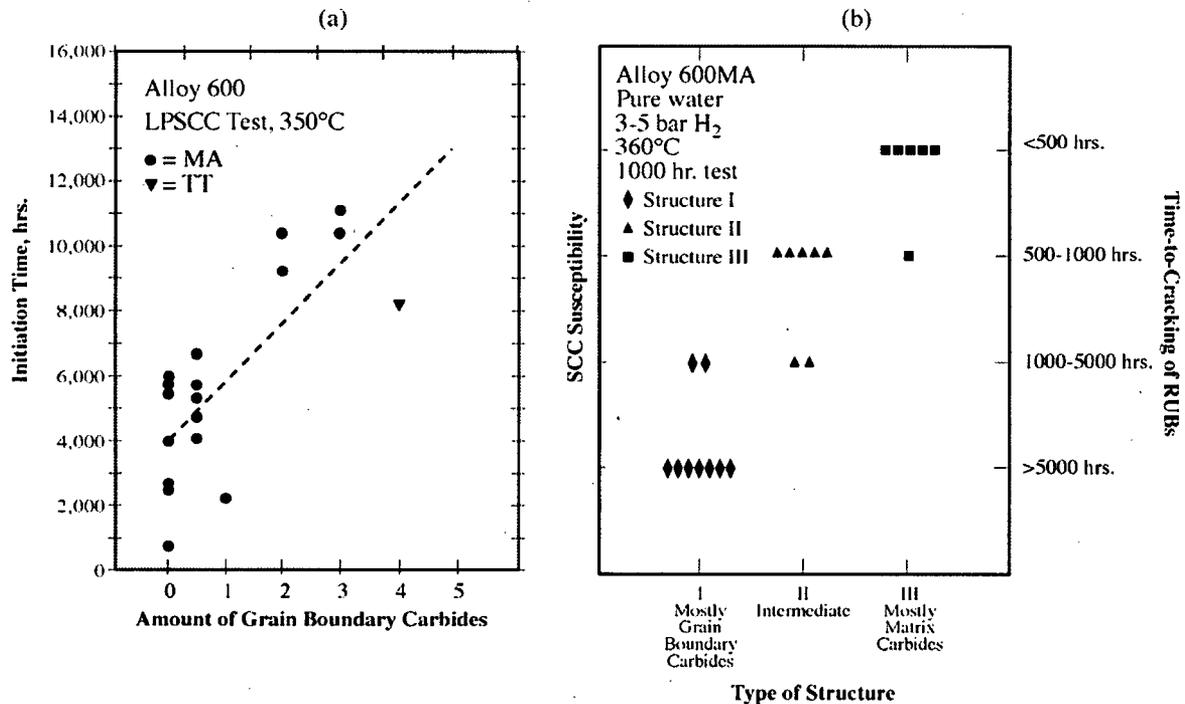
## 6. Temperature

The temperature dependence of LPSCC has been extensively studied, and this work is reviewed by Staehle and Gorman.<sup>1</sup> The most reliable values of the activation energy for initiation seems to be about 40-55 Kcal/mol and for propagation about 30-35 Kcal/mol.

Figure B.7.17 shows some typical data for initiation and propagation from the work of Webb<sup>27</sup> (Figure B.7.17a) and the review by Cassagne et al.<sup>28</sup> (Figure B.7.17b).

## 7. Stress

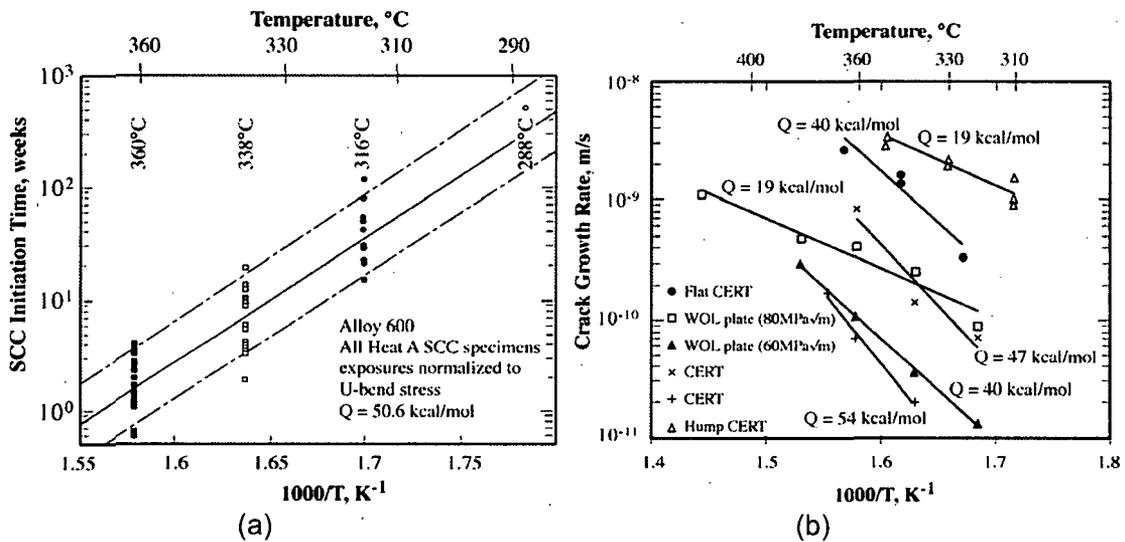
The dependence of LPSCC on stress for Alloy 600MA has also been extensively investigated. Figure B.7.18 shows results from studies of the effects of stress on initiation and propagation, respectively, from Bandy and van Rooyen<sup>33</sup> and Scott.<sup>34</sup> In general, for initiation from smooth specimens the stress required is in the range of the annealed yield stress, with a stress exponent of about 4 as shown in Figure B.7.18a. For propagation, the correlation by Scott has been the most widely used and is shown in Figure B.7.18b.



**Fig. B.7.16** (a) Time-for-initiation vs. extent of grain boundary carbides. From Norring et al.<sup>25</sup> Reprinted with permission from TMS. (b) Relationship between structure and SCC susceptibility. From Gras<sup>29</sup> Reprinted with permission from TMS. Cattant et al.<sup>26</sup>; © 1992 American Nuclear Society. Saint-Paul et al.<sup>30</sup> Courtesy of EDF, and Garriga-Majo et al.<sup>31</sup> © NACE International 1994.

**Table B.7.2**<sup>32</sup> © NACE International 1977  
 Effect of Heat Treatment and Fabrication on Failure at 350°C in Demineralized and Deoxygenated Water. From Blanchet et al.

Metallurgical Condition	Alloy A Alloy 600, C = 0.063 w/o			Alloy B Alloy 600, C = 0.040 w/o			Alloy C Cr 17%, Ni 77%, C = 0.002 w/o	
	As-Received	As-Quenched	Sensitized	As-Received	As-Quenched	Sensitized	As-Received	Sensitized
Determination $\sigma_{max}$ at the outer fiber at 20°C (kg/mm <sup>2</sup> ) ( $\pm 15\%$ )	72	36	72	43	29	43	41	41
Samples cracked after:								
750 hours	0/6	0/3	0/3	0/3	0/2	0/2	6/7	0/5
1500 hours	6/6	0/3	0/3	0/3	0/2	0/2	7/7	3/5
2250 hours	-	0/3	0/3	1/3	0/2	0/2	-	5/5
3000 hours	-	0/3	0/3	2/3	0/2	0/2	-	-
4500 hours	-	1/3	0/3	2/3	0/2	0/2	-	-
8250 hours	-	1/3	0/3	3/3	0/2	0/2	-	-
10000 hours	-	2/3	0/3	-	1/2	0/2	-	-



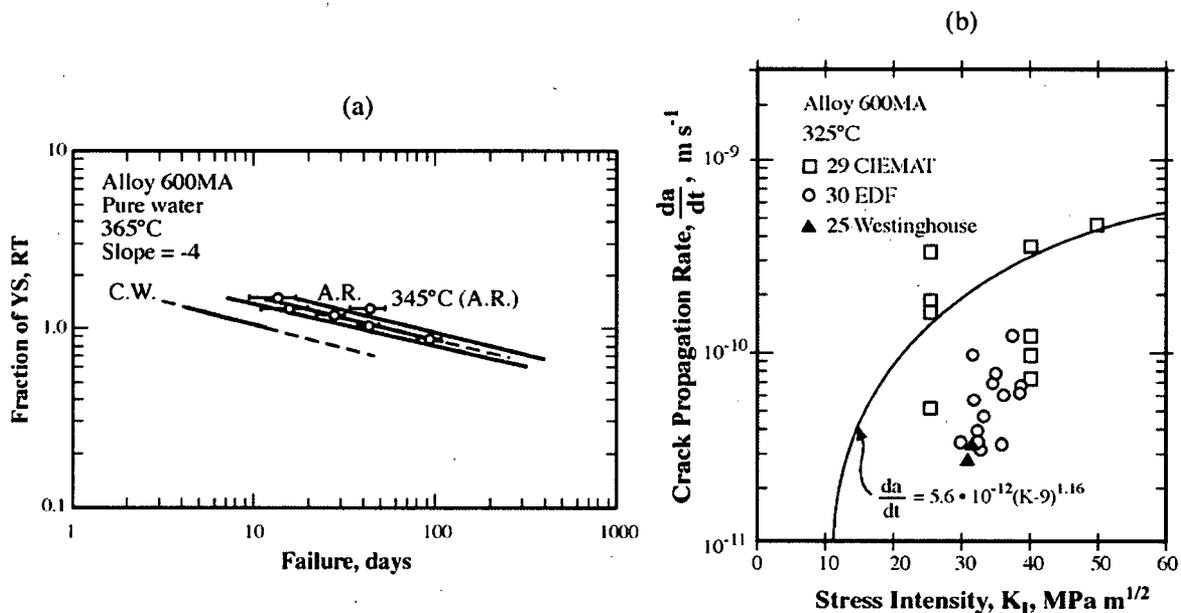
**Fig. B.7.17** (a) SCC initiation time vs. 1000/T for Alloy 600 using U-bend specimens in pure water. From Webb.<sup>27</sup> Reprinted with permission from TMS. (b) Crack growth rate vs. 1000/T for Alloy 600MA from six authors using CERT and WOL type specimens. From Cassagne et al.<sup>28</sup> Courtesy of the European Federation of Corrosion.

## SCC of Alloy 600MA on the OD

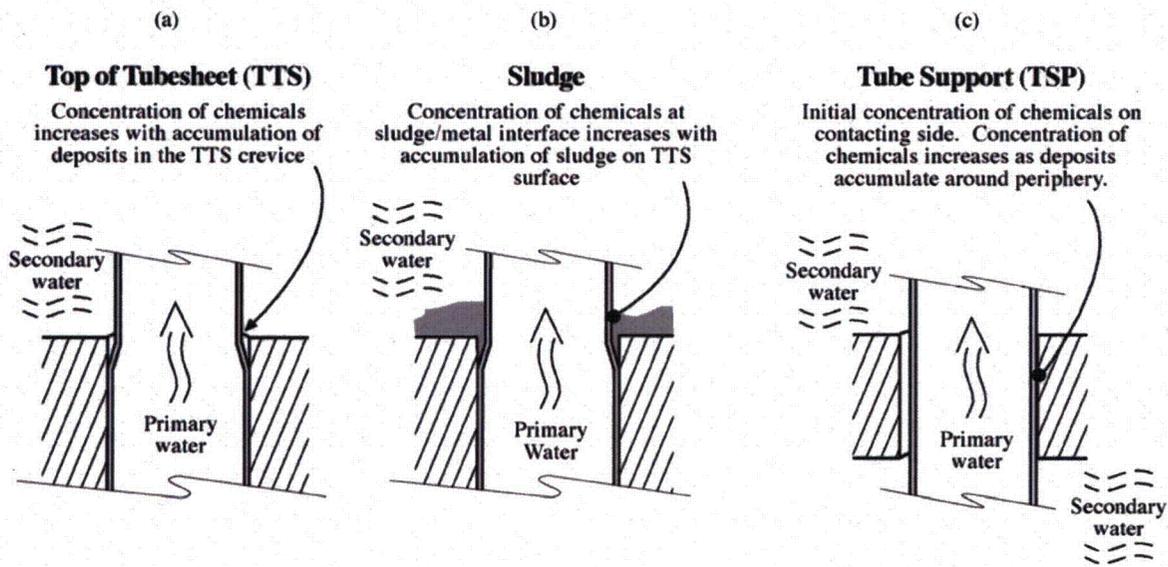
### 1. Geometry, phases, and chemistry

SCC on the OD of SG tubes occurs mainly at locations where impurity chemicals can concentrate due to the local superheat, mainly at tube supports and at the configurational and sludge crevices at the top of tubesheets, as shown in Figure B.7.19. Figure B.7.20<sup>35</sup> shows a schematic view of the complexity and chemistry of these regions of concentration as well the chemicals that typically concentrate and lead to SCC. With time, chemicals accumulate in the heat transfer crevices to produce solids and saturated solutions owing to the superheat. Further, as local transport is stifled by the formation of solids, a steam phase develops. The main intimation here is the complexity of chemical, electrochemical, and physical conditions. Such an array provides many different conditions that can produce corrosion and stress corrosion cracking.

SCC on the OD generally occurs where the superheat is the greatest, and this is mainly on the inlet or hot leg side with the number of affected tubes shown in Figure B.7.21a<sup>36</sup> according to distance from the inlet of the hot side. An indication of the magnitude of concentrations of chemicals in these crevices is given in Figure B.7.21b.<sup>37</sup>



**Fig. B.7.18** (a) Fraction of RT yield stress vs. time-to-failure for Alloy 600MA at 365°C in pure water. Stress exponent about -4. Yield point stresses in the range of 323 to 386 MPa. From Bandy and van Rooyen.<sup>33</sup> (b) Crack propagation rate vs. stress intensity for Alloy 600MA at 325°C. From Scott.<sup>34</sup> © NACE International 1996.



**Fig. B.7.19** Geometries that produce heat transfer crevices involving tubing in steam generators: (a) top of the tubesheet crevice; (b) sludge at the top of the tubesheet; (c) tube support. From Staehle and Gorman.<sup>1</sup> © NACE International 2003/2004.

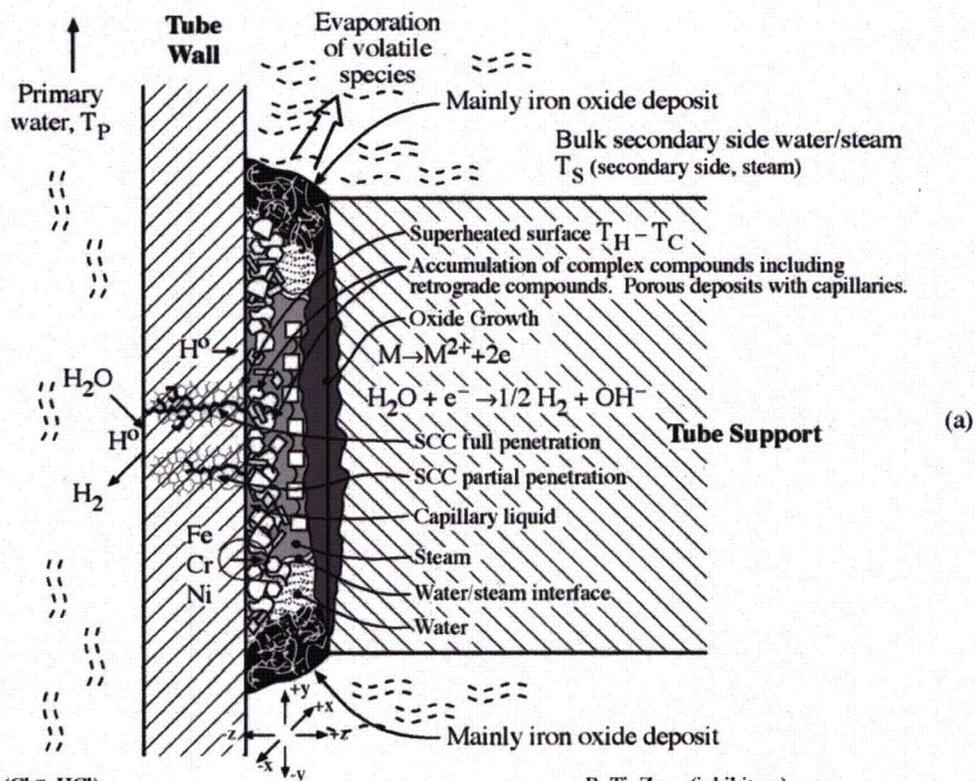
## 2. Surface chemistry--ODSCC is chemistry driven

Some indication of the complexity of the chemistries on the surfaces of tubes is shown in Figure B.7.22, taken from the work of Cattant et al.,<sup>38</sup> where the residual chemistry on the surface of a tube at a tube support region has been analyzed both inside the crevice and outside on the freespan adjacent to the crevice. Figure B.7.23<sup>38</sup> shows the ratio of species inside the crevice to outside on the freespan, indicating that the concentrations, species, and enrichments vary.

## 3. The bulk chemistry

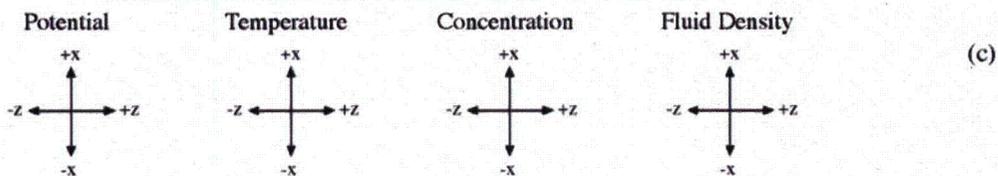
While the chemistries inside the heat transfer crevices provide a variety of possibly corrosive environments, the bulk environment provides important bounding chemistries affecting corrosion:

- a. **Low hydrogen**--The hydrogen concentration on the secondary side is in the range of 1 ppb due to the boiling action removing gases. This low concentration of hydrogen, following the Nernst equation, leads to raising the open circuit potential on the order of 200-250 mV above that on the primary side where there is not boiling and hydrogen is deliberately added at about 3 ppm. A 200-250 mV increase could be sufficient to take the secondary side out of the range of LPSCC.
- b. **Hydrazine (affects potential)**-- $N_2H_4$  is added to the secondary side in concentrations of about 5-100 ppb in order to reduce the oxygen concentration in the recirculating water to <5 ppb. It is also believed by some that additions of  $N_2H_4$  lower the tendency for corrosion to occur in heat transfer crevices. It may also lower the corrosion potential due to the relatively low equilibrium potential for the  $N_2/N_2H_4$  equilibrium. The overall combined effect of low hydrogen and the  $N_2H_4$  on potential is not clear.

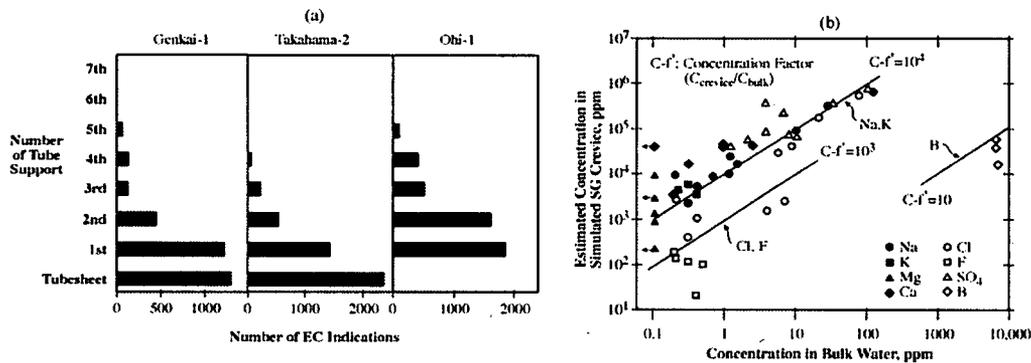


Cl	(Cl $^-$ , HCl)	B, Ti, Zn	(inhibitors)
SO $_x$	(retrograde compounds plus S $^{6+} \rightarrow S^{4+} \rightarrow S^{2+} \rightarrow S^0 \rightarrow S^{2-}$ )	O $_2$	(O $_2$ , H $_2$ O, compounds)
SiO $_x$	(SiO $_2$ , complex compounds)	H $_2$	(H $_2$ , H $^+$ , H $^0$ )
AlO $_x$	(Al $_2$ O $_3$ , complex compounds)	N $_2$ H $_4$	(N $_2$ H $_4$ , NH $_3$ , N $_2$ )
Cu	(Cu $^0$ , Cu $^{2+}$ , CuO)	C	(CO $_3^{2-}$ , organic)
Pb	(Pb $^0$ , PbO $_x^{\pm y}$ )	N	(NO $_x$ , organic)
Na, Ca, Mg	(complex compounds)	Fe, Cr, Ni	(Fe $^{2+}$ , Cr $^{3+}$ , Ni $^{2+}$ , complex compounds)
Na $_2$ HPO $_4$	(retrograde compounds plus H $_3$ PO $_4$ )		

#### Gradients



**Fig. B.7.20** Schematic view of heat transfer crevice at a tube support. (a) Geometry. (b) Chemicals that accumulate and transform. (c) Types of gradients inside the heat transfer crevice. From Staehle.<sup>35</sup>



**Fig. B.7.21** (a) Number of indications at successive tube support locations for three plants using Alloy 600MA after about 12 to 15 years service. From Takamatsu et al.<sup>36</sup> © NACE International 1996. (b) Estimated concentration of species in a simulated SG crevice vs. concentration in the bulk water. Various concentration factors shown. From Takamatsu et al.<sup>37</sup> © 1992 American Nuclear Society.

c. Hydrazine (a reductant)--  $N_2H_4$  produces a second effect as it combines with sulfate impurities reducing them to lower valence and ultimately to sulfides. Sulfides are well known to accelerate the entry of hydrogen and to reduce passivity.<sup>39,40,41</sup>

Thus, there are two important environmental influences that affect the occurrence of corrosion on the secondary side. One is the concentration of chemistry inside heat transfer crevices and the other involves the combined effects of low hydrogen and high hydrazine as they interact with the bulk and the crevice chemicals.

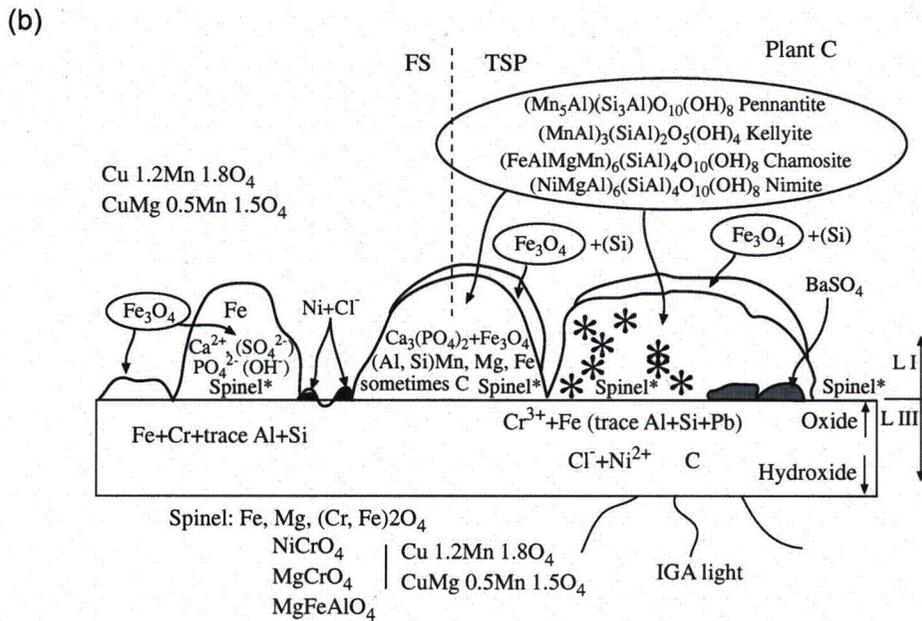
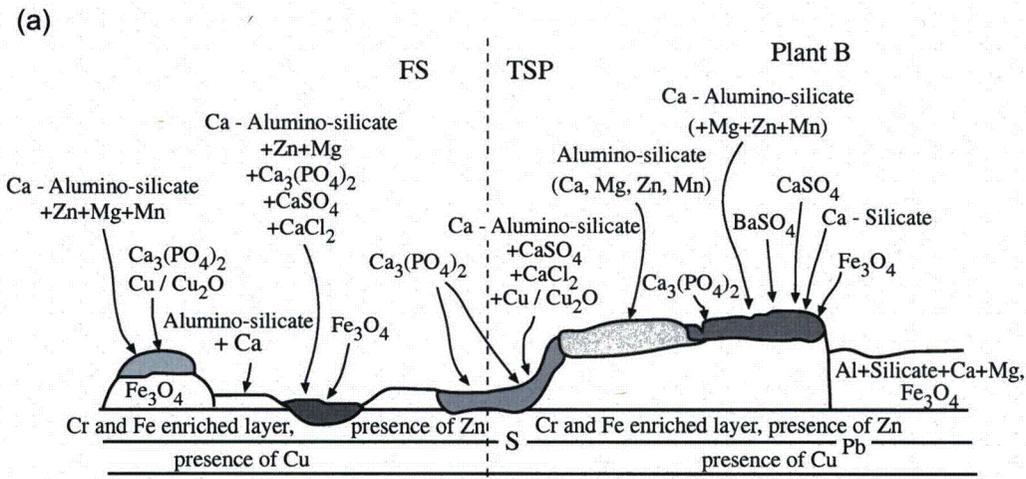
#### 4. Steam phase

Figure B.7.20 suggests that, in addition to the complexity of chemistry, there is also a steam phase in heat transfer crevices. Such local steam conditions and the associated two phase interface have been shown to accelerate SCC in Alloy 600 as reviewed by Staehle and Gorman.<sup>1</sup>

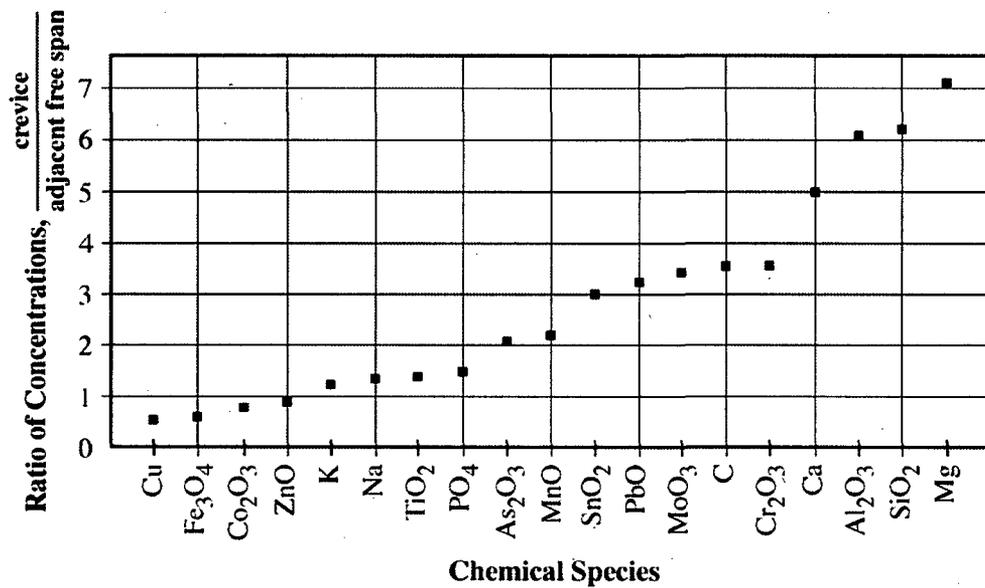
#### 5. Acidic and alkaline chemistries

Aside from the LPSCC on the primary side as discussed in Section 2.2 and the possibility of its occurring on the secondary side, both acidic and alkaline environments have been investigated as being possibly related to the SCC that has occurred in the secondary side. The overall view of AcSCC and AkSCC for Alloy 600MA is shown in Figure B.7.9a as well as in Figure B.7.10a.

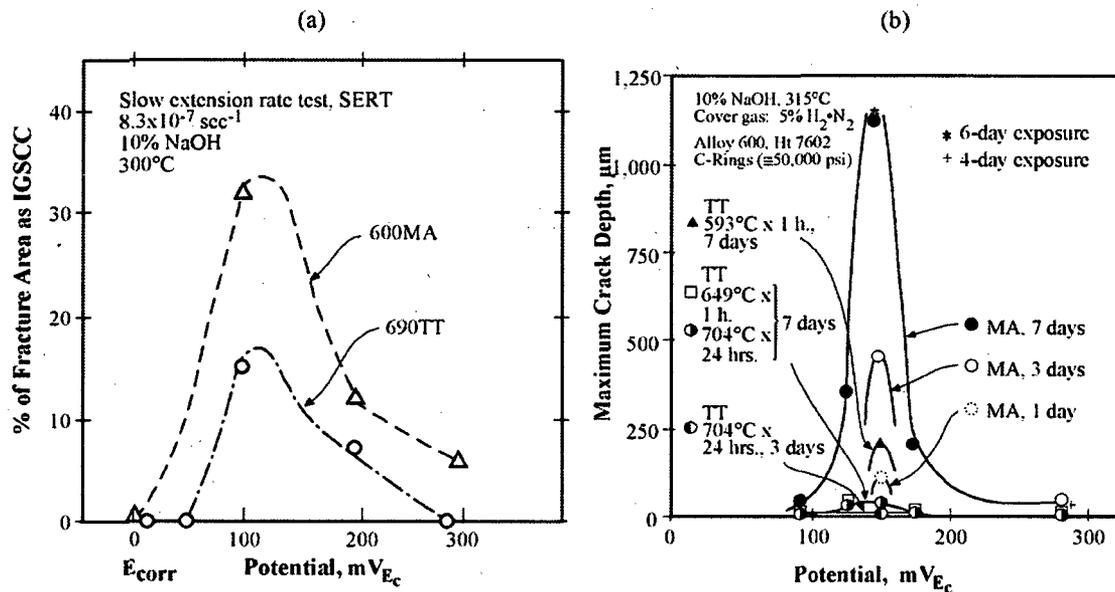
Figures B.7.24a<sup>42</sup> and 24b<sup>43</sup> show the effect of electrochemical potential on SCC in alkaline environments specifically for Alloys 600MA, 600TT and 690TT. Here, it is clear that the three alloys sustain AkSCC in the same range of potential with Alloys 600TT and 690TT being more resistant. Staehle and Gorman<sup>1</sup> discuss AkSCC and its dependencies extensively.



**Fig. B.7.22** (a) Schematic view of the OD of a tube near a TSP showing adjacent regions from inside the TSP and outside on the free surface. The condenser was brass and the water chemistry was morpholine AVT. (b) Schematic view of OD tube surface from TSP 2 showing adjacent regions inside the TSP and outside on the free surface. The condenser was titanium and the water conditioning was  $\text{NH}_3$  AVT. The tube was examined after 79,900 hours. From Cattant et al.<sup>38</sup> Courtesy of EDF & Framatome-ANP.



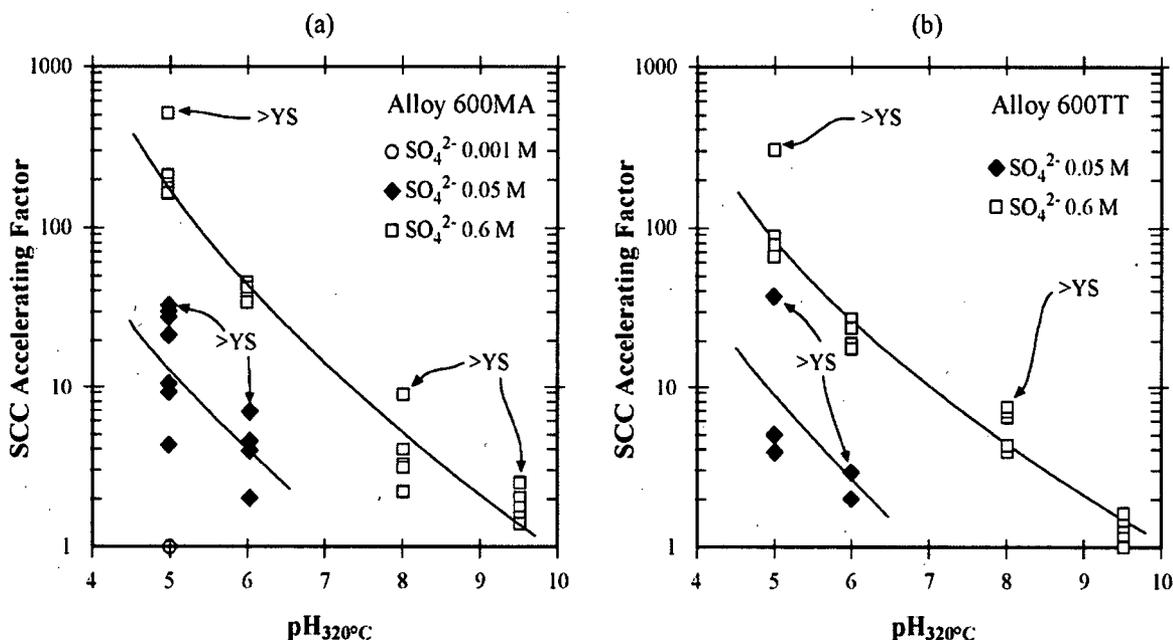
**Fig. B.7.23** Ratio of concentrations of elemental species in deposits from occluded heat transfer crevices vs. those from adjacent free-span surfaces. Species given in ascending order of ratio. Data from 340 pulled tubes. From Cattant et al.<sup>38</sup> Courtesy of EDF & Framatome-ANP.



**Fig. B.7.24** Dependence of IGSCC on applied potential above the deaerated open circuit potential. (a) Percent of fracture area as IGSCC for Alloy 600MA and Alloy 690TT at 300°C as a function of potential in a 10% NaOH solution. From Suzuki.<sup>42</sup> © 1992 American Nuclear Society. (b) Maximum crack depth vs. potential for Alloy 600 exposed in 10% NaOH at 315°C for mill-annealed and various thermal treatments. From Pessall.<sup>43</sup> Reprinted with permission from Elsevier.

Figures B.7.25 and 26 provide insights into AcSCC for Alloys 600MA, 600TT and 690TT and conform also to the patterns noted in Figures B.7.9 and 10. Figure B.7.25<sup>44</sup> shows that the propensity towards AcSCC, when exposed to sulfate anions, decreases with increasing pH, and as expected, continues into the slightly alkaline region for both Alloys 600MA and 600TT.

Figure B.7.26<sup>49</sup> shows the effect of potential on the AcSCC of Alloys 600MA and 690TT also exposed to sulfate anions. Here, the potentials are achieved by adding cupric oxide and by changing the hydrogen concentration. Note in Figure B.7.26c, simply adding copper does not produce significant SCC relative to the CuO. This Figure shows that Alloy 690TT sustains AcSCC but not at normal open circuit potentials; whereas, Alloy 600MA sustains AcSCC regardless of the potentials, although there is an acceleration at pH 4+ at higher potentials.



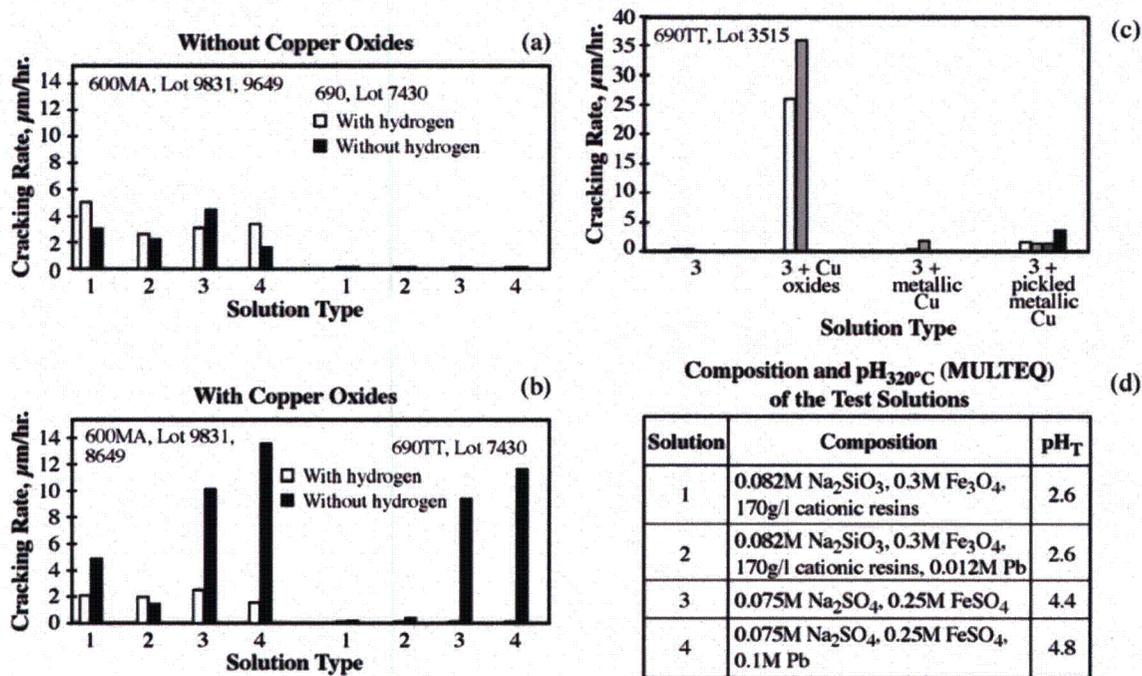
**Fig. B.7.25** SCC accelerating factor vs. pH with different concentrations of SO<sub>4</sub><sup>2-</sup> and with different stresses for (a) Alloy 600MA and (b) Alloy 600TT. Accelerating factor taken from rate of crack initiation at 0.001M (pH<sub>320°C</sub> = 5) being the reference. >YS refers to "two legs touching" condition of the branches of the C-ring; below this stress, specimens were stressed at 0.8 YS and 1.0 YS. From deBouvier et al.<sup>44</sup> Reprinted with permission from TMS.

## 6. Lead chemistries, PbSCC

PbSCC has had varying importance over time. It was first identified as important in the 1965 paper of Copson and Dean<sup>45</sup> and was suggested then as the reason for the SCC observed by Coriou. In this first paper, SCC due to Pb was said to be characteristically TGSCC; since most of the subsequent field observations of SCC exhibited IGSCC, Pb was not considered important, and ODSCC was mainly attributed to AkSCC and to AcSCC.

However, due to the review of Sarver<sup>46</sup> of old work of Copson, it became clear that PbSCC of Alloy 600MA was predominantly IGSCC; whereas, PbSCC of Alloy 600TT, SR (stress relieved), and SN (sensitized) was predominantly TGSCC. This evolution is described by Staehle.<sup>47</sup> Also important are the results from Bruemmer and Thomas,<sup>48</sup> who have shown that as much as 7w/o of Pb occurs in the tips of some SCC taken from SGs. Further, Pb has been observed to concentrate on heat transfer surfaces in many examinations of pulled tubes even where no accidental intrusions of Pb have occurred.

While the proof is not substantial, it is a reasonable speculation that much of the IGSCC on the secondary side, especially after the early concerns about AkSCC and AkIGC, could have been due to Pb.



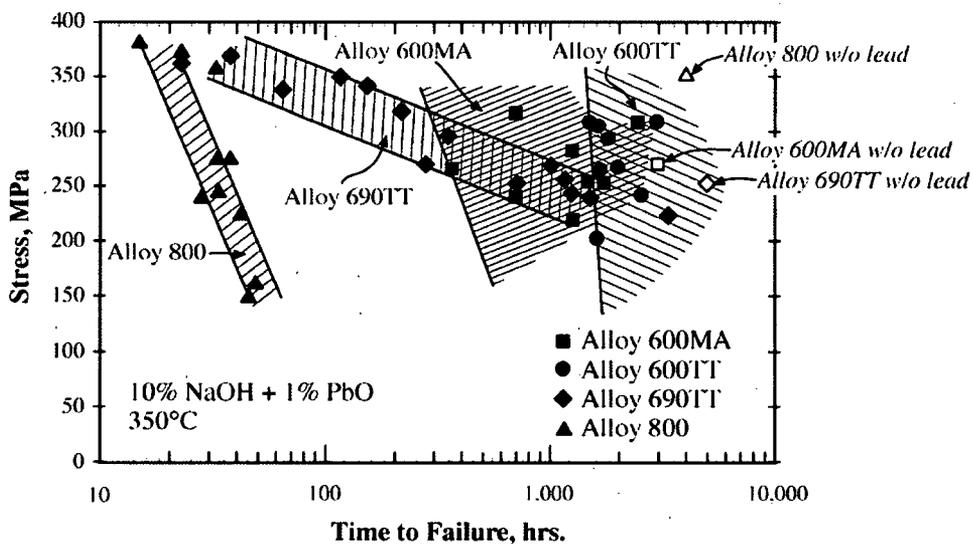
**Fig. B.7.26** (a) Cracking rates for Alloys 600MA and 690TT in acidic solutions without copper oxides with and without 5% H<sub>2</sub> added to argon cover gas in capsules at 320°C. (b) Cracking rates for Alloys 600MA and 690TT in acidic solutions with copper oxides with and without 5% H<sub>2</sub> added to argon cover gas in capsules at 320°C. (c) Cracking rates obtained for Alloy 690TT with solution #3 at 320°C. (d) Compositions of environments. From Pierson and Laire.<sup>49</sup> Courtesy of Laborelec.

The occurrences of PbSCC over the range of pH are shown in Figures B.7.27, 28, and 29. Figure 27<sup>51,52</sup> shows the four alloys in an alkaline solution with and without the presence of Pb. The Pb substantially accelerates the propensity for SCC especially for Alloys 800 and 690TT. At lower pH, which is characteristic of AVT environments, Wright and Mirzai<sup>50</sup> have summarized the results from various authors as a function of Pb concentration as shown in Figure B.7.28. SCC occurs in Alloy 600MA as a function of Pb readily at 1 ppm. However, PbSCC does not seem to occur in Alloy 690TT in this AVT environment. At lower pH in chloride, PbSCC occurs in both Alloys 600MA and 690TT; however, the rate of SCC in Alloy 690TT is lower. At this

lower pH of 4.5 and at 300 ppm Pb, as  $PbCl_2$ , the Alloy 690 sustains SCC and corrodes generally.

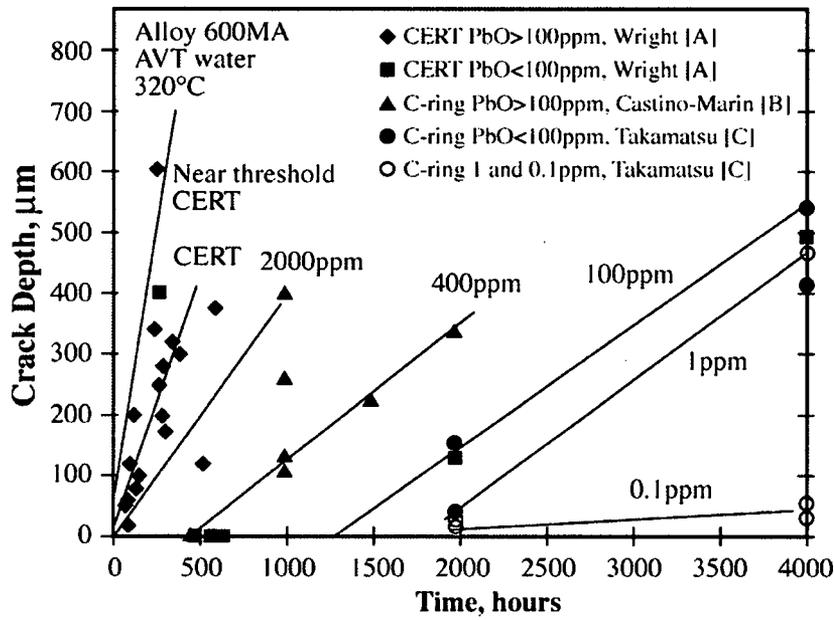
### 7. Low valence sulfur chemistries

Low valences of sulfur-containing anions are important because they can greatly accelerate SCC, at least as shown in the limited work performed to date in alkaline solutions, and because these ions can be produced by the reduction of sulfate ions with hydrazine. Further, from studies at lower temperatures, the lower valence sulfur ions greatly accelerate general corrosion. In particular, the low valence sulfur species accelerate the AkSCC of Alloy 690.

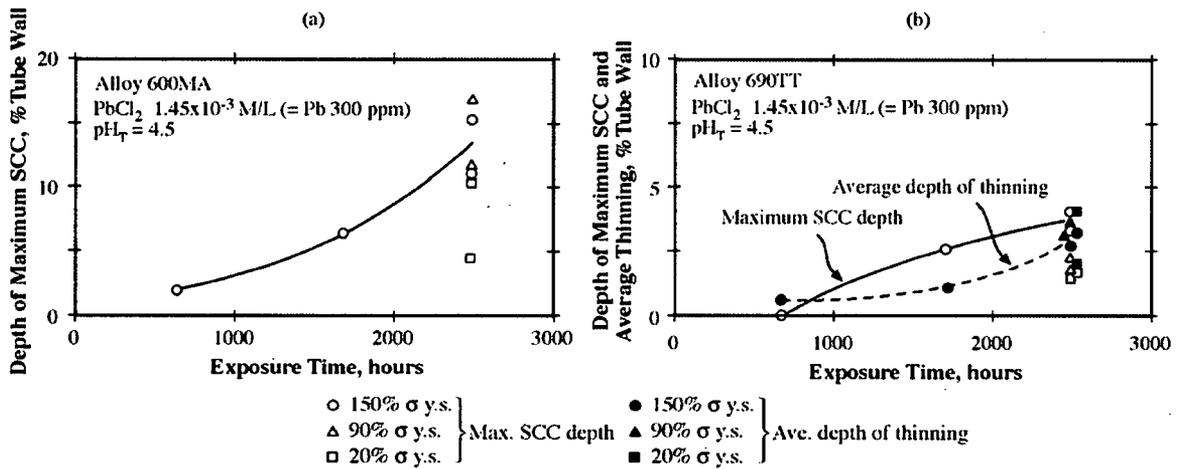


**Fig. B.7.27** Stress vs. time-to-failure of Alloys 600MA and 600TT (two tubes), 690TT (four tubes), and 800 (two tubes) in 10% NaOH + 1% PbO at 350° C. From Vaillant et al.<sup>51</sup> Courtesy of the European Federation of Corrosion. and Rocher et al.<sup>52</sup> Courtesy of EDF & CEA.

Table B.7.3 compares concentrated alkaline solutions with various additions of CuO, PbO,  $S_2O_3^{2-}$ , and  $NaSO_4+FeSO_4$ .



**Fig. B.7.28** Crack depth vs. time data for Alloy 600MA in AVT water at 320°C with various concentrations of PbO. From Wright and Mirzai.<sup>50</sup> Reprinted with permission from TMS. With data from [A] Wright;<sup>53</sup> Reprinted with permission from BNES. [B] Castano-Marín et al.,<sup>54</sup> [C] and Takamatsu et al.<sup>55</sup> © 1997 American Nuclear Society.



**Fig. B.7.29** Depth vs. time for PbSCC at  $\text{pH}_{340^\circ\text{C}} 4.5$  in which various stresses were applied for 2500 hour exposure in water where  $\text{O}_2 < 5$  ppb and Pb was added as  $\text{PbCl}_2$ . From Sakai et al.<sup>56</sup> © 1992 American Nuclear Society. (a) Alloy 600MA at  $1.45 \times 10^{-3}$  M/L of  $\text{PbCl}_2$ . (b) Alloy 690TT at  $1.45 \times 10^{-3}$  M/L of  $\text{PbCl}_2$ . Maximum SCC depth plus average depth of GC.

**Table B.7.3** Results from Visual Examination of Specimens Exposed\* to Alkaline Solutions at 350°C with Added Species (cracked samples/tested samples). From Briceno and Castano.<sup>57</sup> Used by Permission of EPRI.

Material	10% NaOH	10% NaOH + 0.1M CuO	10% NaOH + 0.1 M PbO	50% NaOH + 5% Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.75% M Na <sub>2</sub> SO <sub>4</sub> + 0.25% M FeSO <sub>4</sub>	0.75% M Na <sub>2</sub> SO <sub>4</sub> + 0.25% M FeSO <sub>4</sub>
Alloy 800 7-73243	3/3	3/3	4/4	4/4	4/4	0/4 (3/4)**
Alloy 800SP 81373	15/15	15/15	15/15	15/15	15/15	11/15 (15/15)**
Alloy 690TT WF816T	0/15	0/15	15/15	14/14	0/15	1/15
Alloy 690TT 764408	0/15	0/15	15/15	15/15	0/15	0/15
Alloy 600MA 1450	8/9	0/9 (2/9)**	0/9 (3/9)**	2/9	6/9 (8/9)**	9/9

\* 500 hours exposure; C-ring specimens; 2% strain.

\*\* Visual examination after bending the samples.

**Table B.7.4** Results of Cathodic Polarization Scans in 50% NaOH with 5% Additions at 316°C. Courtesy of P. King.<sup>58</sup> Private communication.

5% Addition	Alloy 600		Alloy 690	
	Worst Case	Observations	Worst Case	Observations
Na <sub>2</sub> CO <sub>3</sub>	No difference*	General attack	No difference*	Slight g.b. intrusions
Na <sub>2</sub> S	TT ring	Heavy general attack	MA C-ring	TGSCC
NaHS	No difference	Heavy general attack	MA C-ring	TGSCC
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	No difference	Heavy general attack	MA C-ring	TGSCC
Na <sub>2</sub> SO <sub>4</sub>	No difference	Slight general attack	MA C-ring	Slight g.b. intrusions

\* No difference indicates no substantial difference between ring or C-ring specimens for mill-annealed and thermally-treated condition.

MA - Heat treatment not defined

TT - Mill annealed plus 704°C /16 hrs

TGSCC - Transgranular stress corrosion cracks



In addition to this work directly from operating plants, Figure B.7.31 from the work of Jacko<sup>59</sup> shows that Alloy 600TT is improved relative to Alloy 600MA in about the same proportions as the results in Figure B.7.30. Here, Alloy 690 exhibits no LPSCC.

## 2. Alkaline as AkSCC

In alkaline solutions the propensity for AkSCC in Alloy 600TT is less than Alloy 600MA as shown in Figures B.7.10b and 10d. Figure B.7.32<sup>7</sup> shows that the plateau crack velocity of Alloy 600TT is a 5-10 times less than for Alloy 600MA in 4 and 100 g/l NaOH solutions.

## 3. Acidic as AcSCC

Depending on the data, Alloy 600TT exhibits improvements compared to Alloy 600MA. Figure B.7.33<sup>61</sup> shows significant improvements over a range of acidic pH in sulfate solutions.

## 4. Lead

The work of Miglin and Sarver,<sup>60</sup> which covered a broad range of pH with Pb additions, showed that Alloy 600TT was generally, but not substantially, improved over Alloy 600MA.

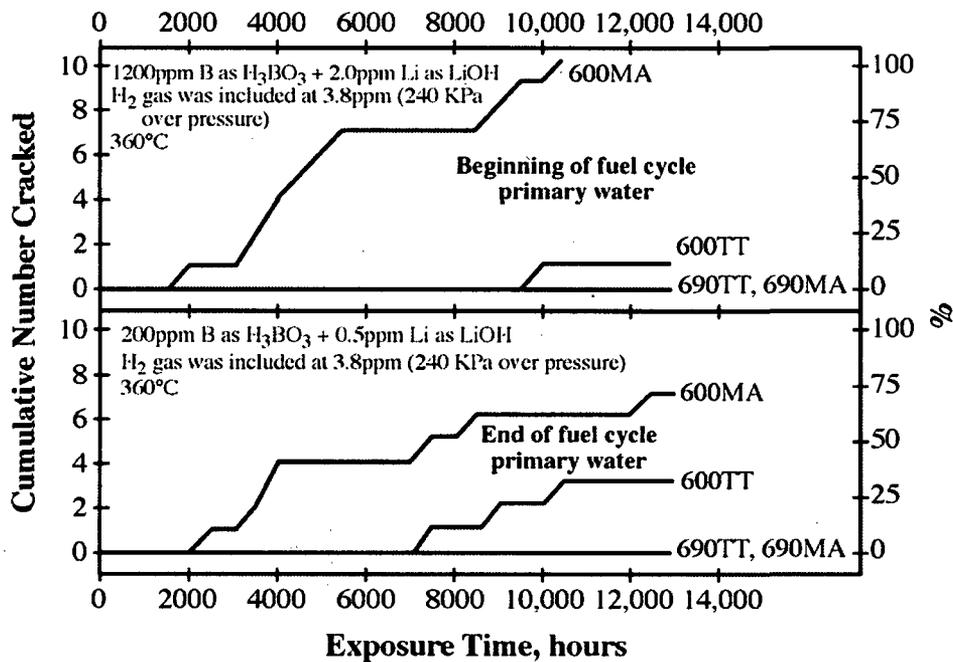


Fig. B.7.31 Cumulative number of Alloy 600 and 690 specimens exposed for 13,000 hours in chemistries typical of the (a) beginning of life and (b) end of life for a fuel cycle. From Jacko.<sup>59</sup> Used by Permission of EPRI.

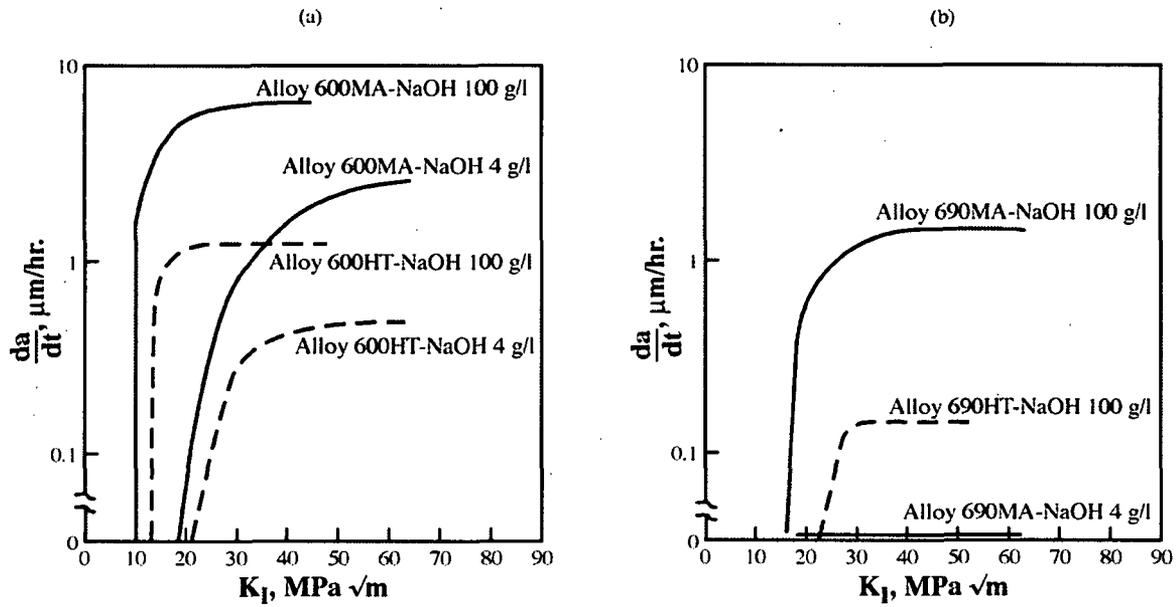


Fig. B.7.32  $da/dt$  vs.  $K$  for Alloys 600 (a) and 690 (b) exposed to various concentrations of NaOH at 350°C with a WOL type specimen. HT corresponds to 700°C for 16 h. From Berge and Donati.<sup>7</sup> © 1981 American Nuclear Society.

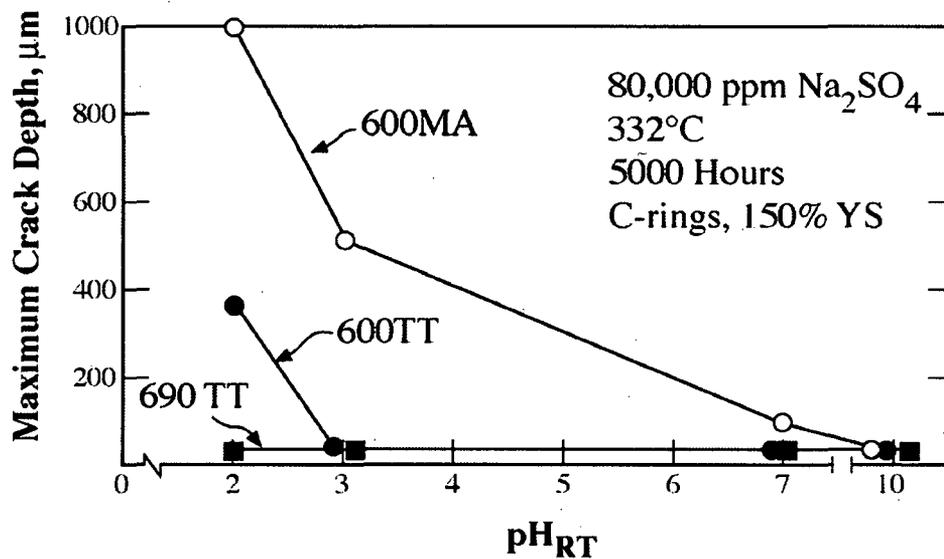
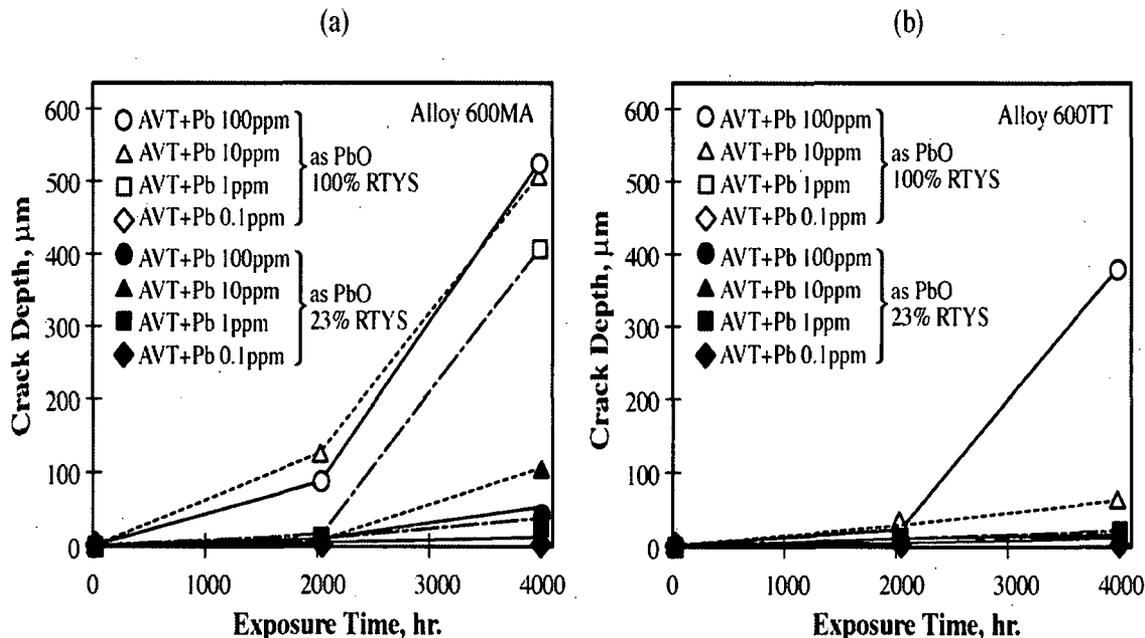


Fig. B.7.33 Maximum crack depth vs. room temperature pH for Alloy 600MA, Alloy 600TT, and Alloy 690TT exposed in acidic sulfate solutions at 332°C for 5000 hours as C-rings stressed to 150% of the yield strength. From Smith et al.<sup>61</sup> © 1986 American Nuclear Society.

Figure B.7.27 shows that Alloy 600TT is improved relative to Alloy 600MA possibly by a factor of five in time-to-failure, but there are no significant differences in the stress threshold.

In AVT environments, as shown in Figure B.7.34,<sup>55</sup> Alloy 600TT is improved, compared to Alloy 600MA, and does not support SCC at such low concentrations of Pb. However, Alloy 600TT is not significantly better at higher concentrations.



**Fig. B.7.34** Crack depth vs. time for various concentrations of Pb at two stresses and for Alloys 600MA and 600TT in deaerated AVT water containing 0.26 ppm NH<sub>3</sub>+0.1ppm N<sub>2</sub>H<sub>4</sub>. From Takamatsu et al.<sup>55</sup> © 1997 American Nuclear Society.

### 5. Sulfur

There appear to be no data for the SCC of Alloy 600TT in solutions which contain low valence sulfur.

### Alloy 690 TT

As it became clear that Alloy 600 would undergo degradation and cracking during the service life of steam generators, work had begun, at least by 1970, to develop an improved alloy as reported by Copson et al.<sup>62</sup> and Flint and Weldon.<sup>63</sup> This work involved evaluating alloys in three environments: highly oxygenated environments with double U-bend crevices, lead environments, and alkaline environments. Sensitized and non-sensitized alloys were studied, and a relatively large range of iron and chromium additions to a nickel base were evaluated.

Alloy 690TT is now becoming the standard material for use in SG tubing, where it has so far provided excellent service performance, as well as for welding and for thick sections where substantial corrosion resistance, together with compatibility of the thermal expansion coefficient with adjacent low alloy steel components, is required, as shown in Figure B.7.5.

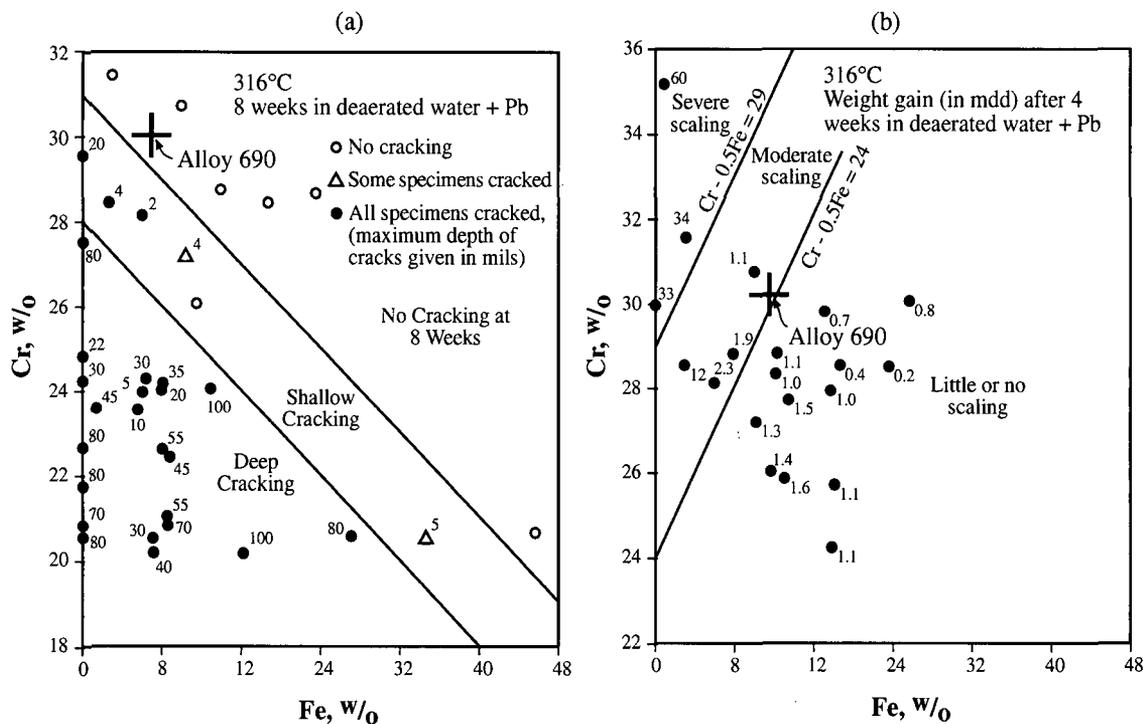
From these early tests, the highly oxygenated solutions were not particularly useful from the point of view of PWR applications, except perhaps for the unknown conditions inside crevices.

However, the testing in the Pb-containing solutions proved to be of great interest in later years as shown in Figure B.7.35.<sup>46</sup>

Figure B.7.35 shows the combined effects of iron and nickel both on the SCC and scaling of alloys exposed to high temperature water containing Pb. Both figures show the locations of the Alloy 690 composition. These results showed that Alloy 690 composition is close to a scaling condition (severe general corrosion) and to SCC in Pb environments. Regardless, the Alloy 690 composition seemed to be an optimum as shown in Figure B.7.35, and the testing in the Pb-containing solutions foresaw, unintentionally, the importance of Pb on the secondary side. In the following years development of these high chromium alloys continued and intensified in the late 1970s and early 1980s.

### 1. Primary water as LPSCC

The improvement of Alloy 690TT over Alloy 600MA, as well as over Alloy 600TT, is shown in Figure B.7.31 where laboratory testing was carried out for about 13,000 hours at 360°C.



**Fig. B.7.35** (a) Maximum depth of SCC of Ni-Cr-Fe alloys after 8 weeks in deaerated water plus Pb at 316°C. (b) Weight gain of Ni-Cr-Fe alloys after 4 weeks in deaerated water plus Pb. From Sarver et al.<sup>46</sup> Used by Permission of EPRI.

### 2. Alkaline as AkSCC

Figure B.7.32 for crack growth rate vs. stress intensity shows that the plateau velocity for Alloy 690 is a factor of 10-100 less than for Alloy 600MA depending on the concentration of NaOH.

The overall mapping of SCC for the three alloys of 600MA, 600TT, and 690TT in Figure B.7.10 shows that Alloy 690TT is improved and the threshold of pH for the onset of AkSCC is higher.

### 3. Acidic as AcSCC

Figure B.7.26 shows that Alloy 690TT at open circuit in sulfate solutions does not sustain AcSCC. This is similar to the pattern for Figure B.7.10. However, with Figure B.7.26 it appears that Alloy 690TT does sustain significant AcSCC, but at potentials that may exceed the normal open circuit range depending on what potentials are actually present in crevices and that results from the very low hydrogen on the secondary side.

### 4. Lead as PbSCC

The extensive work of Miglin and Sarver, which is discussed by Staehle and Gorman<sup>1</sup> and by Staehle,<sup>35</sup> shows that Alloy 690 is improved, in terms of resistance to PbSCC, over both Alloy 600MA and Alloy 600TT until pH 9.9 is reached, at which point the SCC of Alloy 690TT is significant, especially in steam (implying easy vapor phase transport of Pb). Figure B.7.27 reflects this greatly increased sensitivity of Alloy 690 in alkaline solutions.

While Figure B.7.26 shows that sulfates seem to inhibit PbSCC of Alloy 690TT in acidic solutions, Figure B.7.29b shows the Pb as  $PbCl_2$  promotes PbSCC, although at a rate about 1/5 that for Alloy 600MA.

### 5. Sulfur as $S^y$ SCC

Tables B.7.3 and 4 show that the presence of low valence sulfur either as a  $-2$  (sulfide) or  $+2$  (thiosulfate) increases the susceptibility to  $S^y$ SCC for Alloy 690TT relative to Alloy 600MA.

## **Alloy 800**

Figure B.7.4 from Coriou et al.<sup>13</sup> based on the general trends of his observations, suggests that the composition of Alloy 800 as shown in Figure B.7.2 and Table B.7.1 would resist SCC in both pure water and chloride-containing water, although Copson and Cheng's work in Figure B.7.3 suggests that Alloy 800 is within the domain of chloride SCC. Such SCC of commercial grade Alloy 800 in chloride solutions was also observed by Staehle et al.<sup>64</sup> for commercially available materials at the time.

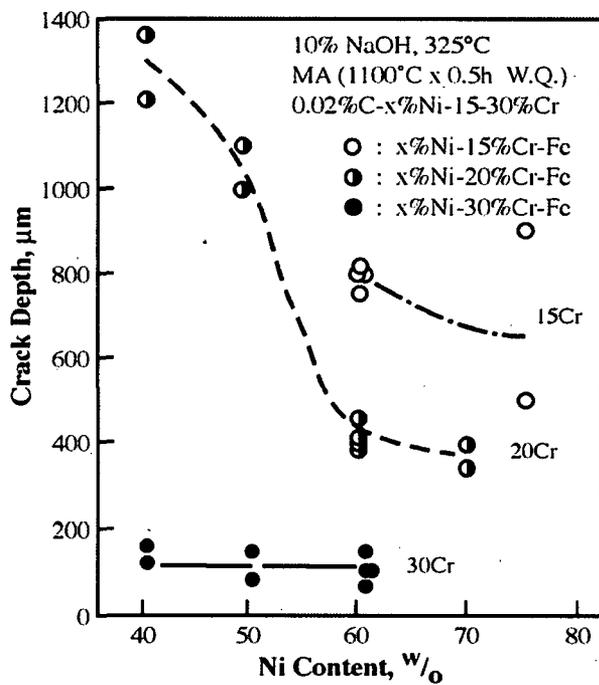
Mainly based on the work of Coriou plus internal work, Siemens chose a controlled version of Alloy 800 for their steam generators, and this alloy has exhibited excellent in-service performance.

### 1. Primary water as LPSCC

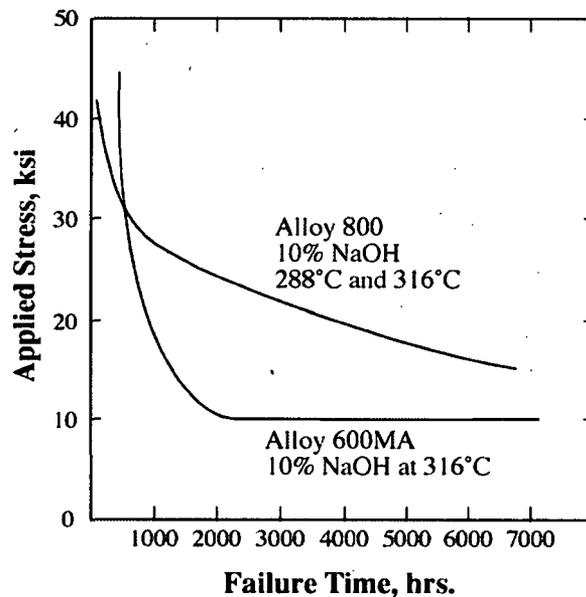
The dependence of LPSCC on nickel concentration was reported by Coriou et al.<sup>65</sup> They showed that the nickel concentration of Alloy 800 was below the Ni concentration that would permit LPSCC. Later Nagano et al.<sup>66</sup> showed that Alloy 800 was equivalent to Alloy 690 as shown in Figure B.7.36.

Since the first observation of Coriou in his schematic assessment in Figure B.7.4, Alloy 800 has remained resistant to LPSCC.

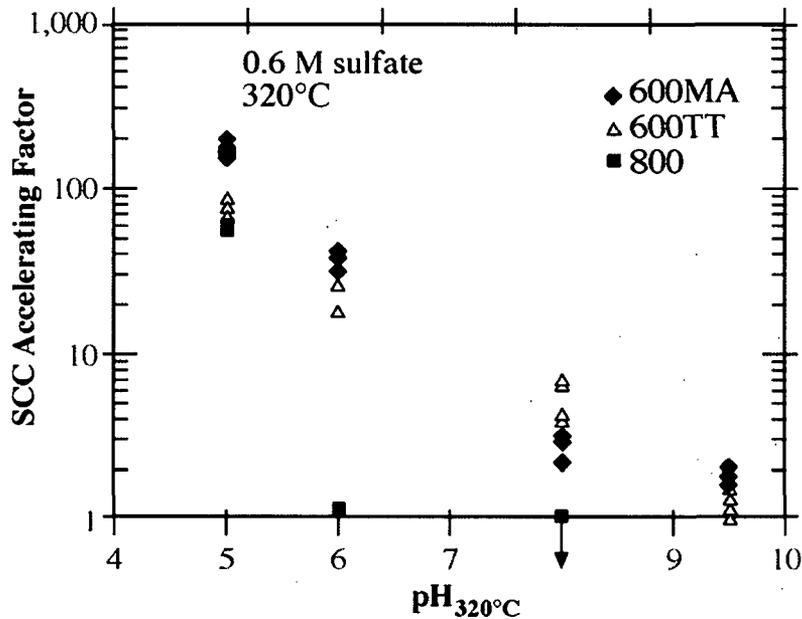




**Fig. B.7.37** Crack depth vs. Ni concentration for Ni-Cr-Fe alloys + 0.02%C exposed in a deaerated 10% NaOH solution at 325°C for 200 hours as single U-bends. Specimens mill annealed. From Nagano et al.<sup>67</sup> Used by Permission of EPRI.



**Fig. B.7.38** Stress vs. time for Alloy 800 in 10% NaOH at 288 and 316°C, and for Alloy 600MA in 10% NaOH at 316°C. From Wilson et al.<sup>68</sup> © 1975 ANS.



**Fig. B.7.39** SCC accelerating factor vs. pH for three alloys in 0.6M sulfate environments at 320°C. Accelerating factor taken from the rate of crack initiation at 0.001M (pH<sub>320°C</sub> =5) being the reference. 150% YS refers to the “two legs touching” condition of the branches of the C-ring; below this stress, specimens were stressed at 0.8 YS and 1.0 YS. From deBouvier et al.<sup>44</sup> Reprinted with permission from TMS.

#### 4. Lead

Alloy 800 seems to be the least resistant of the Alloys 600MA, 600TT, 690TT and 800 in alkaline solutions containing Pb as shown in Figure B.7.27. Despite the relative trends, more recent electrochemical studies by Y. Lu of AECL have shown the standard SG Alloy 800 is generally resistant to PbSCC in alkaline solutions.<sup>69</sup>

#### 5. Sulfur

Table B.7.3 shows that Alloy 800 is similarly prone to SCC in S<sup>y-</sup> SCC (alkaline base) as Alloy 690 in alkaline solutions. There appear to be no other data for other ranges of pH for any of the alloys.

### **Conclusions**

1. The early choice of Alloy 600MA for tubing in PWR steam generators together with drilled hole tube supports, less pure secondary water chemistry, and relatively high residual stresses produced extensive failures of tubing leading to the eventual replacement of many steam generators tubed with Alloy 600MA. This choice of Alloy 600MA was based on a set of assumptions and laboratory testing that turned out not to be valid under the operating conditions of tubes in steam generators.

2. A set of mitigations has reduced, for the present, the rate of SCC on the primary and secondary sides of SG tubes associated with Alloy 600MA. These mitigations have included:

- Using better alloys including Alloy 600TT, Alloy 690TT, and Alloy 800.
- Using line contact tube supports and changing the materials of the tube supports to stainless steel.
- Improving the secondary water chemistry.
- Reducing residual stresses.
- Improved methods of inspection.

3. The potential for secondary-side degradation and cracking still exists:

- Pb and S impurities.
- Acidic crevices, especially with chloride.
- Longer time and significant accumulation of impurities in line contact tube supports.
- Denting and increased stresses at the top of the tubesheet.
- Possible large releases of sequestered lead resulting from subtle changes in water chemistry, perhaps due to a still further increase in purity of the boiler water.
- Nucleation of SCC at locations of dings, dents, and scratches.

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