

INFLUENCE OF STARTUP OXIDIZING TRANSIENTS ON IGA/SCC IN PWR STEAM GENERATORS

J. A. Gorman,¹ A. R. McIlree,² T. Gaudreau,² L. Björnkvist,³ and P.-O. Andersson³

ABSTRACT

There is a considerable amount of evidence that oxidizing conditions during and following startups are an important factor in the intergranular corrosion/stress corrosion cracking (IGA/SCC) of mill annealed alloy 600 steam generator tubes. This evidence includes plant data that indicate that the growth of IGA/SCC correlates better in some cases with numbers of startups than with time at power, laboratory tests in several plausible crevice environments that show that small amounts of copper oxides accelerate the rate of IGA/SCC, laboratory tests that show that elevating the electrochemical potential (ECP) increases the rates of IGA/SCC in many chemical environments, and laboratory tests that show that copper oxides, hematite, and other oxidized corrosion products can raise the ECP of several solution chemistries into aggressive ranges. Some preliminary data also exist that show that some amounts of oxidized species are produced during typical layup and startup conditions, but data for the subsequent reduction of these oxides are largely lacking. The purpose of this paper is to review the available evidence, to arrive at conclusions regarding the probable importance of oxidizing conditions during startup on occurrence of IGA/SCC, and to identify needed research to better quantify the situation.

1. Dominion Engineering, Inc., McLean, Virginia, USA
2. Electric Power Research Institute, Palo Alto, California, USA
3. Vattenfall, Ringhals plant, Väröbacka, Sweden

INFLUENCE OF STARTUP OXIDIZING TRANSIENTS ON IGA/SCC IN PWR STEAM GENERATORS

J. A. Gorman, A. R. McIlree, T. Gaudreau, L. Björnkvist, and P.-O. Andersson

INTRODUCTION

Secondary side intergranular attack/stress corrosion cracking (IGA/SCC) of mill annealed alloy 600 tubes is a major problem in pressurized water reactor (PWR) steam generators. For units operating on all volatile water chemistry, this mode of tube degradation was first noted in about 1971 in two early European plants, Beznau 1 and Obrigheim.^{1,2} It was first seen in the USA in about 1977 in units with deep tube sheet crevices.³ Since that time IGA/SCC has been increasing steadily around the industry despite extensive research into possible causes and many remedial actions. It is currently the dominant reason for tube repair and steam generator replacement in the United States.⁴

Remedial measures taken against IGA/SCC have included implementing stringent secondary water chemistry controls that have resulted in large reductions in the ingress of impurities into the steam generators. Many other remedies have also been implemented, including (1) increases in concentrations of oxygen scavengers and elimination of copper alloys from secondary systems in efforts to try to ensure that aggressive oxidizing potentials do not develop in the steam generators, (2) use of buffers such as boric acid and inhibitors such as titanium dioxide to minimize corrosion due to caustics that might develop in crevices, and (3) control of molar ratios of cations and anions in the feedwater in efforts to ensure that impurities that concentrate in crevices do not form strong caustics or acids. It is believed that application of these remedies has helped to reduce the rate of IGA/SCC in many plants. However, despite these efforts, the IGA/SCC problems continue to increase.

The balance of this paper reviews the factors involved in IGA/SCC, evaluates those that could be causing the continued occurrence of IGA/SCC despite application of remedial measures, and discusses the evidence that indicates that oxidizing conditions occurring during startups and early periods of operation after shutdowns may be an important factor in this corrosion.

CAUSES OF IGA/SCC

The causes of IGA/SCC in mill annealed alloy 600 tubing are generally evaluated in terms of the classical three factors of stress corrosion: material, environment and stress. The results of extensive research regarding these three factors for mill annealed alloy 600 tubing of the type used in steam generators are briefly summarized below, together with brief discussions of implications for thermally treated alloy 600 tubing.

Material Susceptibility

Laboratory tests indicate that the susceptibility of mill annealed alloy 600 tubing to IGA/SCC is affected by its microstructure, especially the distribution of carbides, which in turn depends on the thermo-mechanical processing used in the manufacture of the tubing. Early research indicated that susceptibility in pure water and caustic environments was associated with a material microstructure with few intergranular carbides at grain boundaries and copious carbides in the matrix of the grains.⁵ However, as industrial experience has continued to accumulate and test results have been obtained for additional environments, it has become evident that mill annealed alloy 600 is susceptible to IGA/SCC in a variety of environments. While its microstructure has a strong influence in some specific environments, especially pure and primary water, the microstructures of essentially all of the mill annealed alloy 600 tubing in service result in substantial susceptibility of the tubing in one or more of the possible secondary side environments.

Tests and service experience indicate that susceptibility of alloy 600 to IGA/SCC, in addition to being affected by microstructure, is strongly increased by local cold work. For example, severe IGA/SCC is often associated with lines of abrasion or scratches. In addition, laboratory tests show that cold worked surface layers of abraded tubes experience much more rapid IGA/SCC than regions below the cold worked layer.^{6,7} Further, crack growth rate tests show that SCC grows much more rapidly in cold worked material than in non cold worked material.⁸

The situation with respect to thermally treated alloy 600 tubing appears to be that it is susceptible to IGA/SCC in the same manner as mill annealed tubing, but not to the same extent. Tests in a variety of environments, and limited service experience, indicate that thermally treated alloy 600 tubing is less susceptible to IGA/SCC than mill annealed alloy 600 tubing but is not immune.⁹

The important points with respect to this paper are that (1) all of the mill annealed alloy 600 tubing in service probably is susceptible to IGA/SCC in secondary side crevice environments that can develop in well run PWR steam generators, and (2) it is likely that thermally treated alloy 600 is also susceptible, but to a lesser degree.

Stress

Many tests show that susceptibility to SCC increases as the total stress at the surface increases. In pure and primary water environments, susceptibility seems to only occur for stresses above about the elastic limit, e.g., above about 80% of the 0.2% strain yield strength. In more aggressive environments, e.g., lead containing environments, caustic environments, and acidic environments, susceptibility to SCC is exhibited at least down to stresses as low as 10 ksi (70 MPa) (typical pressure induced hoop stress) and IGA is sometimes observed even in the presence of compressive stresses. The main conclusion with respect to this paper is that mill annealed alloy 600 tubes in PWR steam generators have surface stresses in many locations that are sufficiently high to lead to IGA/SCC. Because of lower surface residual stresses, thermally treated tubing has lower

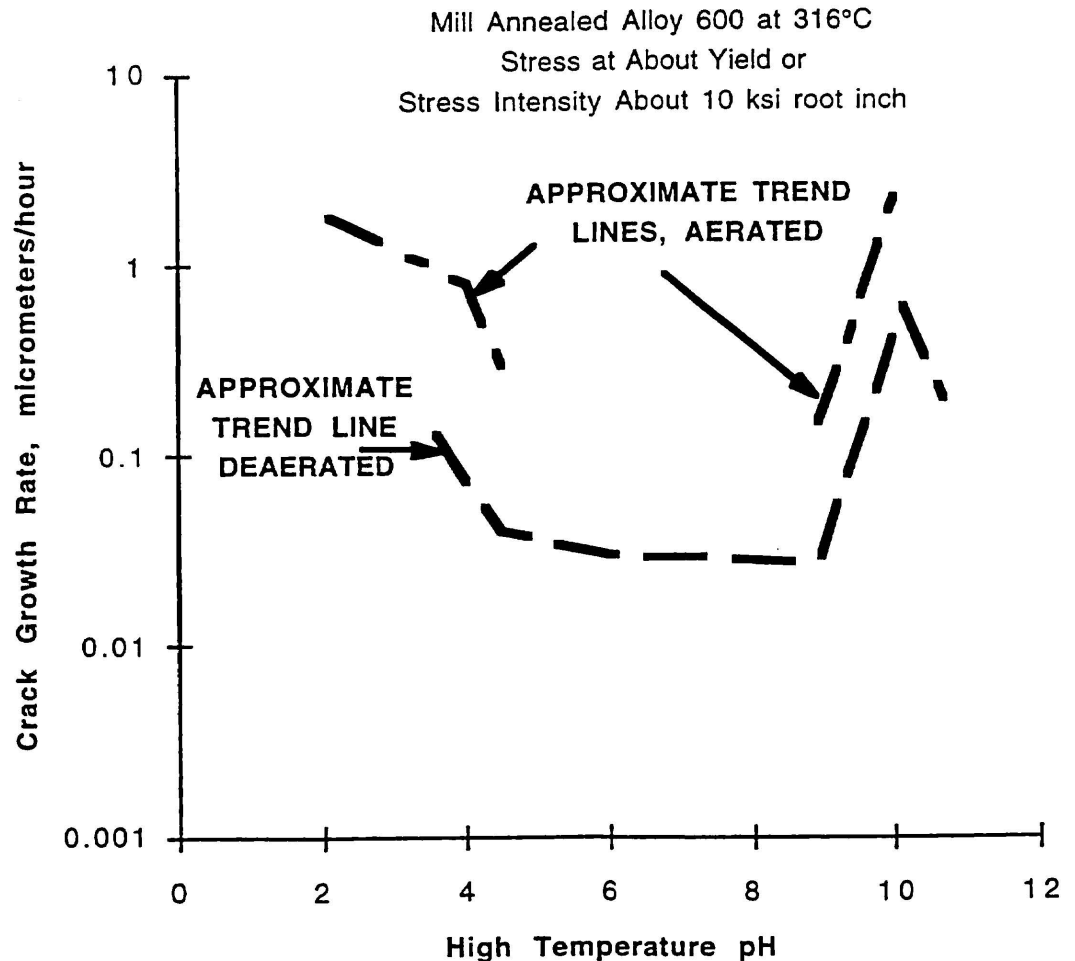
susceptibility than mill annealed tubing, but probably is not immune, especially in regions such as expansion transitions at the top of the tube sheet where there are both local cold work and moderately high residual stresses from the expansion process.

Environment

The effects of many environmental factors on IGA/SCC of alloy 600 have been determined by laboratory tests.¹⁰ In summary, these show that:

- Temperature. Test data show that increasing temperature leads to increasing rates of IGA/SCC in a variety of environments, including primary water, caustic, and acidic environments, with apparent activation energies ranging from 30 to 70 kcal/mole. Evaluations of plant data indicate that increases of temperature increase rates of IGA/SCC by about an apparent activation energy of 54 kcal/mole.¹¹ IGA/SCC has been limited in units operating with hot leg temperatures below 590°F (310°C), but has been relatively severe in some units operating at 590°F (310°C), e.g., Kewaunee.¹² Higher temperature units, especially of the preheater type, have sometimes exhibited rapid and severe IGA/SCC.
- pH. Tests show that pH below about 5 and pH above about 9.5 lead to accelerated rates of IGA/SCC, including both initiation and growth of flaws. The effect of pH on growth rate of SCC is shown in Figure 1.¹³ The growth rates shown in Figure 1 could imply that pH in the range of 5 to 9 has a reduced impact on the continued growth of already initiated SCC, and that electrochemical potential could be the dominant factor.
- Electrochemical Potential (ECP). Tests show that at low and high pH, even small increases in ECP (e.g., 100 to 150 mV) above the open circuit potential in deaerated solutions lead to rapid increases in IGA/SCC (e.g., see Figure 1).^{14,15,16} The effect of increased potential in the near neutral region has not been well explored. However, one test in a lead contaminated environment showed that an increase of 130 mV due to the presence of copper oxide caused SCC, whereas no SCC initiation was observed without the copper oxide.¹⁷ In addition, recent crack growth rate tests using thick compact tensile specimens indicate that increasing the potential strongly increases the crack growth rate in complex environments at pH 8 and 10.¹⁸
- Deleterious Species. Tests indicate that the presence of small concentrations of lead strongly increase susceptibility to IGA/SCC.^{19,20} Reduced sulfur species also appear to have similar effects.^{21,22,23} Other species may also have deleterious effects. For example, extensive evaluations of removed tube samples and related tests indicate that alumino silicate gels that can form in crevice areas provide locations where organics or other species can accumulate and cause the breakdown of protective chromium oxides and lead to the occurrence of IGA/SCC.²⁴ On the other hand, recent evaluations of plant data by Westinghouse indicate that silica in the secondary water may reduce the rate of IGA/SCC.²⁵

Figure 1. Crack Growth Rate versus pH



In summary with regard to environmental effects on IGA/SCC of alloy 600, it is clear that many variables affect the initiation and growth, and that the lowest rates of occurrence correlate with: (1) low temperature, (2) pH in the near neutral to mildly alkaline range, (3) ECP near the reversible hydrogen line (essentially at the free corrosion potential in fully deaerated solutions), and (4) freedom from deleterious species such as lead and reduced sulfur species. It is also clear that the rate of IGA/SCC is sensitive to small changes in environmental parameters, with perhaps the greatest sensitivity being associated with small changes in the ECP. Unfortunately, determining and controlling the ECP in crevice areas is difficult, especially for startup and transient conditions.

OCCURRENCE OF IGA/SCC IN WELL MANAGED PLANTS

Recommended water chemistry practices have been developed considering the results of corrosion research and plant experience and are documented in EPRI's Secondary Water Chemistry Guidelines.²⁶ Essentially all western style PWR plants with alloy 600 tubing operate in accordance with these guidelines. Despite this careful operation, some units are experiencing rapid IGA/SCC. This has occurred despite the following:

- Control of water chemistry such that deleterious species are kept to low levels. The success of this effort has been confirmed by evaluation of deposits and oxides from crevice areas that show that deleterious species, especially lead, are generally at low levels. For example, lead is generally in the range of 100 - 1,000 ppm of deposits. It is not known whether these levels are enough to aggravate IGA/SCC, nor how they correspond to the ~1 ppm of the water level of lead that tests indicate can cause attack,²⁷ but they are well below the much higher levels known to cause rapid attack in plants. Impurity levels of species such as Na^+ , Cl^- , and $\text{SO}_4^{=}$ typically have been controlled in the low to sub ppb range in the blowdown.
- In some of the plants, use of on-line boric acid additions, which tests indicate should neutralize any caustics that form in crevices. The ability of boric acid to neutralize caustic in the field is more difficult and may not be achieved.
- Operation with water chemistry that hideout return evaluations indicate have kept the pH in crevice areas in the near neutral range.
- Operation with high hydrazine levels (>100 ppb) that are expected to keep the ECP low during normal power operation.

In summary, the water chemistry improvements and remedial actions described above are considered to have reduced the severity of the IGA/SCC experienced by plants. However, severe IGA/SCC continues to occur in some well managed units despite application of many remedial actions and predicted benign conditions in the crevice areas where the IGA/SCC is occurring (i.e., predicted near neutral, low ECP conditions and low levels of deleterious species).

POSSIBLE NEGLECTED FACTOR

The inability to explain the continued occurrence of severe IGA/SCC despite apparently benign conditions in the crevice areas where it is occurring during normal power operation has led the authors of this paper to conclude that other factors must be controlling the corrosion, and to hypothesize that the most likely of these possible other factors is high oxidizing potentials during startup and early periods of operation after shutdowns. The reasons for coming to this hypothesis include:

- Small increases in oxidizing potential cause large increases in IGA/SCC in several environments where tests have been performed. Tests show this to be the case in caustic environments, acidic environments, and lead contaminated neutral environments.^{28,29,30} It may also be the case in other near neutral environments, but systematic tests in these environments have not been performed.
- Measurements of ECP show that the presence of small concentrations of oxidized corrosion products such as copper oxide and hematite can raise the ECP by the amounts that tests show have strong effects on rates of IGA/SCC, e.g., by 100 mV or more.^{31,32,33}
- Tests in caustic, acidic, and lead contaminated near neutral environments show that small concentrations of copper oxide strongly increase the rate of IGA/SCC.^{34,35,36} This is presumed to be a result of the increase in ECP caused by the copper oxide.
- In many plants, much of the secondary system is exposed to oxidizing conditions during long shutdowns. In addition, at many plants the secondary sides of steam generators are often exposed to moist air for several weeks or even months during shutdowns, and sometimes to air saturated water. The exposure to moist oxidizing conditions undoubtedly results in oxidation of corrosion products and metal surfaces for much of the secondary system surface area, including in the steam generators. Further, during startups and early operation, it is likely that significant amounts of oxidized corrosion products are introduced into the steam generators from the secondary system. Unless plant startup procedures ensure the reduction of these oxidized materials to a fully reduced state before power operation, they may raise the ECP in crevice areas to aggressive levels during the startup - early operation period following a long shutdown, i.e., until the oxidized corrosion products (e.g., hematite and copper oxide) are fully reduced. Remedial measures taken at Kori 1, which included a deliberate corrosion potential reduction hydrazine soak, resulted in a demonstrated benefit.³⁷ However, since a total of four remedial measures were implemented at the plant, it is impossible to categorically assign a benefit to each remedial measure.
- Studies of the occurrence of IGA/SCC in Belgium led researchers at Laborelec to conclude that the growth of cracks in steam generator tubes correlates better with the number of shutdowns and startups than with the length of steady operation.³⁸ This pattern has also been observed at other plants, but has not been well documented. The Belgian researchers speculated that this might be the result of oxidation of copper and other species during shutdowns, and have published reports that even alloy 690 tubing could be damaged by copper oxides.³⁹
- The occurrence of IGA/SCC at two PWRs with preheater steam generators in Sweden has been much less severe than at three domestic units with similar preheater steam generators and slightly younger ages.⁴⁰ Comparison of the plants indicates that temperature cannot explain the difference, since two of the three

domestic units have operated most of their lives at lower temperatures than the Swedish units. Material and stress factors also do not appear likely to be the explanation, since the tubing for all five units was made by the same manufacturer, and the steam generator design and tube installation procedures are similar. Water chemistry during power operation seems unlikely to be the explanation since all five units have been carefully managed in accordance with industry guidelines, and detailed reviews of their water chemistry histories have not revealed any factors related to normal power operation that can explain the differences in corrosion experience. Materials of construction of the secondary system also seem unlikely to be the explanation, since two of three domestic units do not have any copper alloy heat exchangers, similar to the Swedish units. However, one area of significant difference in water chemistry history has been identified: control of oxidizing conditions during layup and startup, as discussed further below.

Significantly more stringent practices have been used at the Swedish units than at the domestic units during secondary system layup and steam generator layup to minimize oxidation of surfaces and to minimize introduction of oxygenated water into the steam generators during startup. For example:

- Forced dry air circulation has been used in both the secondary system and in the steam generators during dry layup at the Swedish units. This has not been done in the domestic units, which typically have left equipment in the "as-is" condition after draining.
- Periods of dry layup of the steam generators have been shorter in the Swedish units since the policy there is to return to wet layup as soon as possible following maintenance that requires draining. The practice at the domestic units has generally been to leave units in the drained condition for long periods.
- Auxiliary feedwater used during shutdown and startup in the Swedish units typically is in the 10 - 30 ppb oxygen range. Domestic units have had difficulties meeting 100 ppb limits and sometimes have had to introduce water with much higher concentrations of oxygen.
- Main feedwater during startup in Swedish units has consistently been below a 100 ppb limit. Some domestic units have difficulties meeting this limit at very low power levels.

Quantifying the effects of the above differences between the Swedish and domestic units on the rates of IGA/SCC is not practical. It is possible that some other unidentified factor explains the much lower rate of IGA/SCC in the Swedish units. However, on balance, the authors consider that the difference in control of exposure to oxidizing conditions during layup and startup is a possible or even likely explanation.

- Evaluation of a TSP crevice removed from Ringhals 3 showed that a gap of 4 to 140 μm existed between the deposits in the crevice and the tube OD.⁴¹ This gap was possibly opened up by differential thermal contraction during cooldown. This type of gap at TSP crevices appears to provide access for oxygen to oxidize the crevice areas during layup periods.

CONCLUSIONS

Evaluations of the large differences in the rate of IGA/SCC at similar preheater units indicates that they are not caused by differences in materials, stresses, temperatures, or water chemistry during normal power operation. However, lower rates of IGA/SCC correlate with the use of significantly more stringent controls during shutdowns and startups to minimize oxidizing conditions during layups and subsequent startups. This observation, coupled with the large increases in rates of IGA/SCC during laboratory tests caused by even small increases in oxidizing potential, leads to the hypothesis that a likely explanation of the rapid IGA/SCC observed in some well managed domestic plants is the occurrence of oxidizing conditions during startups and operating periods immediately following shutdowns.

The observation in Belgium and elsewhere that the occurrence of IGA/SCC seems to correlate better with the number of startups than with the length of operation provides support to the idea that conditions during startups and operating periods immediately following shutdowns are a likely important factor involved in occurrence of IGA/SCC.

The oxidizing conditions that possibly may cause accelerated IGA/SCC during startups and early power operation are believed to be the result of corrosion products and metal surfaces that become oxidized during layup. In the case of the steam generator, these oxidized materials are often developed at the locations where corrosion is observed, i.e., in crevice areas and sludge piles. In the case of the secondary system, the oxidized materials form throughout the secondary system and tend to be swept into the steam generators during startup as secondary system flow velocities increase.

In accordance with water chemistry guidelines, efforts are made to develop reducing conditions in steam generators during startup and power operation by use of hydrazine additions. However, establishing reducing conditions takes considerable periods of time in test loops and autoclaves (many hours or even days) and must take considerably longer in steam generators. In addition, establishing reducing conditions in crevice areas is especially difficult since hydrazine is volatile and does not accumulate in crevices. Thus, once power levels are sufficient to cause steam blanketing to develop in crevices, it may be difficult to reduce the oxidized material that has been formed in the crevices during layup or which deposits in the crevices during startup. Since tests show that IGA/SCC occurs about as rapidly in contaminated steam as in contaminated liquid, crevices with oxidizing materials seem likely to be areas of high susceptibility.

The authors recommend that tests be performed to explore and verify the hypothesis put forward by this paper. Until and unless tests show that the hypothesis is incorrect, the authors conclude that it would be prudent to operate plants assuming that it is correct, i.e., utilities should consider adopting stringent layup and startup controls to minimize oxidizing conditions similar to those used at the Swedish units as discussed above. This recommendation is considered applicable to plants with both mill annealed and thermally treated alloy 600 tubing.

¹ H. J. Shenk, "Investigation of Tube Failures in Inconel 600 Steam Generator Tubing at KWO Obrigheim," Materials Performance, v15, n3, p25-33, March 1976.

² H. Baschek and E. Sandona, "The Steam Generator Failure History of Beznau Nuclear Power Plants I and II," presented at the "Fourth Educational Seminar on Inservice Inspection and Quality Assurance During Operation: Colloquium on Steam Generator Tubing," hosted by Southwest Research Institute, San Antonio, TX, April 22-26, 1974.

³ B. L. Dow, Jr., Steam Generator Progress Report, Revision 3, EPRI, December 1987.

⁴ B. L. Dow, Jr., Steam Generator Progress Report, Revision 13, EPRI TR-106365-R13, EPRI October 1997.

⁵ G. J. Theus and R. H. Emanuelson, Stress Corrosion Cracking of Alloy 600 and Alloy 690 in All Volatile treated Water at Elevated Temperatures, EPRI NP-3061, May 1983.

⁶ R. J. Jacko, Corrosion Evaluation of Thermally Treated Alloy 600 Tubing in Primary and Faulted Secondary Water Environments, EPRI NP-6721-SD, June 1990.

⁷ W. H. Cullen and M. J. Partridge, Susceptibility of Alloys 600 and 690 to Acidified Sulfate and Chloride Environments, EPRI TR-104045, June 1994.

⁸ T. Cassagne and A. Gelpi, "Crack Growth Rate Measurements of Alloy 600 in Steam Generator Tubing in Primary and Hydrogenated AVT Water," Proceedings of the Sixth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, p679, TMS, 1993.

⁹ A. R. McIlree and C. E. Shoemaker, "Material Selection and Alternative Designs for Steam Generators," Steam Generator Reference Book, Chapter 24, EPRI TR-103824, 1994.

¹⁰ Ibid.

¹¹ J. A. Gorman, "Correlation of Hot Leg Temperature with Rate of Steam Generator Tube Corrosion," draft report for EPRI, Feb. 1993.

¹² B. L. Dow, Jr., Op. Cit., EPRI TR-106365-R13, EPRI October 1997.

¹³ PWR Secondary Water Chemistry Guidelines - Revision 3, EPRI TR-102134, Revision 3, May 1993.

¹⁴ R. Bandy, Mechanisms of Intergranular Attack and Stress Corrosion Cracking of Alloy 600 by High-Temperature Caustic Solutions Containing Impurities, EPRI NP-5129, July 1987.

¹⁵ W. H. Cullen and M. J. Partridge, Op. Cit., EPRI TR-104045, June 1994.

¹⁶ B. Bussert, "Round Robin Stress Corrosion Testing of Alloy 600 Split Tube U-Bends," Proceedings: 1991 EPRI Workshop on Secondary-Side Intergranular Corrosion Mechanisms, A10-1 to A10-16, EPRI TR-101103, August 1992.

¹⁷ B. Bussert, Op. Cit., EPRI TR-101103, August 1992.

¹⁸ M. T. Miglin, et al., "SCC of Alloy 600 in Complex Caustic Environments," Proceedings of the Seventh International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, p277-290, NACE, 1995.

¹⁹ H. Takamatsu, et al., "Study on Lead-Induced Stress Corrosion Cracking of Steam Generator Tubing Under AVT Water Chemistry Conditions," Proceedings Eighth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, p216-223, ANS, 1997.

²⁰ A. K. Agrawal and J. P. N. Paine, "Lead Cracking of Alloy 600," Steam Generator Reference Book, Chapter 15, EPRI TR-103824, 1994.

- ²¹ T. Sakai, et al., "Effect of Reduced Sulfur on High Temperature Aqueous Corrosion for Alloy 600," Proceedings of the Fourth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, p12-37 - 12-49, NACE 1990.
- ²² P. Combrade, et al., "Influence of Impurities on the Corrosion of Alloy 600 in High Temperature Water," Proceedings, 1991 EPRI Workshop on Secondary-Side Intergranular Corrosion Mechanisms, EPRI TR-101103, Aug. 1992.
- ²³ B. Sala and P. Combrade et al., "Chemistry of Sulfur in High Temperature Water Reduction of Sulfates," Proceedings of the Fifth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, p502-510, ANS, 1992.
- ²⁴ B. Sala, et al., "The Use of Tube Examinations and Laboratory Simulations to Improve the Knowledge of Local Environments and Surface Reactions in TSPs," Control of Corrosion on the Secondary Side of Steam Generators, p483-497, NACE, 1996.
- ²⁵ A. J. Baum, et al., "Development of Improved PWR Secondary Water Chemistry Guidelines," Proceedings Eighth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, p74-79, ANS, 1997.
- ²⁶ PWR Secondary Water Chemistry Guidelines - Revision 4, EPRI TR-102134Rev4, Nov. 1996.
- ²⁷ H. Takamatsu, et al., Op. Cit., 1997.
- ²⁸ R. Bandy, Op. Cit., EPRI NP-5129, July 1987.
- ²⁹ W. H. Cullen and M. J. Partridge, Op. Cit., EPRI TR-104045, June 1994.
- ³⁰ B. Bussert, Op. Cit., EPRI TR-101103, August 1992.
- ³¹ H. Nagano, "Effects of Environmental and Metallurgical Factors on the IGA/SCC of Alloy 600," Proceedings: 1991 EPRI Workshop on Secondary-Side Intergranular Corrosion Mechanisms, A11-1 to A11-13, EPRI TR-101103, August 1992.
- ³² R. J. Jacko, Op. Cit., EPRI NP-6721-SD, June 1990.
- ³³ B. Bussert, Op. Cit., EPRI TR-101103, August 1992.
- ³⁴ R. J. Jacko, Op. Cit., EPRI NP-6721-SD, June 1990.
- ³⁵ E. Pierson, et al., "Stress Corrosion Cracking of Alloys 690, 800, and 600 in Acid Environments Containing Copper Oxides," Corrosion 96, Paper No. 119, NACE.
- ³⁶ B. Bussert, Op. Cit., EPRI TR-101103, August 1992.
- ³⁷ I. S. Hwang and I.-G. Park, "Control of Alkaline Stress Corrosion Cracking of PWR Stem Generator Tubing," submitted for publication in Corrosion January 1998.
- ³⁸ J. Stubbe and P. Hernalsteen, "Is Corrosion Dependent on the Duration of In-Service Cycle?" Proceedings of the International Symposium Fontevraud III. Contribution of Materials Investigation to the Resolution of Problems Encountered in Pressurized Water Reactors, p365-373, SFEN 12-16 Sept. 1994.
- ³⁹ L. zur Nedden, "Effect of Simulated Outage Conditions in Acid Environment Containing Copper on Corrosion of Steam Generator Tubes," Proceedings Eighth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, p91-99, ANS, 1997.
- ⁴⁰ J. E. Harris, et al., Ringhals Unit 4 - Steam Generator Tube Life Prediction Analysis, private DEI report for Vattenfall, DEI-492, Revision 0, March 1997.
- ⁴¹ A. M. Lancha, "Characterization of Ringhals 3 TSP Crevice and Tube Deposits," Proceedings Eighth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors, p27-34, ANS, 1997.

DISCUSSION

Authors: J.A. Gorman, A.R. McIlree, T. Gaudreau, L. Björnkvist, P.-O. Andersson, Dominion Engineering, Inc., Electric Power Research Institute, and Vattenfall, Ringhals Plant

Paper: Influence of Startup Transients on IGA/SCC in PWR Steam Generators

Questioner: P.J. Prabhu

Question/Comment:

Comment: An alternate or possibly complementary explanation for the excellent performance of Ringhals 3 & 4 SGs with regard to ODSCC could be the boric acid treatment of the secondary side water and high silica concentration in blowdown.

Question: What is the source of the 54 kcal/mole activation energy for ODSCC?

Response:

Our evaluation of plant data indicates that boric acid has some minor beneficial effect in IGA/SCC. We have not investigated the influence of silica, nor any synergistic effect in conjunction with silica.

The source of the 54 K_{cal}/mole activation energy value is given in the paper (reference 11).

Questioner: J. Daret, CEA

Question/Comment:

On the da/dt versus pH plot you presented, the rates on acidic and alkaline sides are unrealistic, even for non-aerated conditions. On the other hand, most utilities consider their crevice conditions are in the 5 - 9.5 pH range, where the dangerous situation could be (according to T. Gendron presentation on internal oxidation) to shift the potential towards the hydrogen lines. If this is the case, is it not dangerous to recommend reducing conditions?

Response:

The da/dt rates shown reflect reported test data. They are for relatively severe conditions of stress, stress intensity, and temperature, and thus are higher than typically seen in plants. However, the pattern they reflect - higher growth rates at low and high pH, and lower growth rates at intermediate near neutron pH - is considered correct.

Limited test data, as cited in the paper, indicate that higher potential in the near neutral range accelerates IGA/SCC, similar to the way it does an acidic and caustic pH conditions. It is important that this be confirmed (or disproven) as soon as possible.

Questioner: F. Vaillant

Question/Comment:

What do you propose, in the field of R&D or analysis of plant operating conditions, to verify the detrimental effect on IGA/SCC of oxidizing conditions during shutdown and startup?

Response:

- (1) Tests to measure the effect of oxidizing corrosion products on the ECP of alloy 600 in a variety of near neutral environments.
- (2) Crack initiation and growth rate tests in near neutral environments with and without oxidizing corrosion products and with and without applied ECPs.
- (3) Detailed evaluations of individual plant IGA/SCC data to determine if IGA/SCC rates are higher for cycles with increased exposure to startup oxidants. (Similar approach to that being used by Laborelec for evaluation of Tihange 3 experience.)

Questioner: R.W. Staehle

Question/Comment:

- (1) It seems that the use of da/dt on the ordinate of the da/dt vs. pH plot is misleading since the SCC of SG tubes is entirely under initiation control. This may give a misleading impression.
- (2) With respect to the desirability of adding hydrazine to reduce SCC, this applies mainly to alkaline SCC since this sub-mode occurs at potentials above the deaerated open circuit. However, in the acid range of pH, this dependence is probably different especially if LPSCC may be occurring and especially since Pb and Cu SCC occur at the deaerated open circuit. The Cl SCC at the mid range may occur at both deaerated open circuit and at higher potential.

Response:

- (1) The da/dt data of Figure 1 mainly came from C-ring tests and thus reflect both initiation and growth. It is believed that both initiation and growth follow similar patterns; faster at low and high pH and slower at near neutral mid-range pH. Thus, the figure is not misleading with respect to its main purpose which is to indicate the pH range with lowest IGA/SCC susceptibility.
- (2) As discussed in the paper, available test data indicate that increases in potential in all three pH ranges - caustic, acidic and near neutral - increase rates of IGA/SCC. It is recognized

that low potentials can also accelerate cracking in some ill-defined situations. On balance, it is considered that risks from oxidizing conditions are more serious than those from reducing conditions and that hydrazine regimes should be selected primarily to avoid exposure to oxidizing conditions.

