An Investigation of the Mechanism of IGA/SCC of Alloy 600 in Corrosion Accelerating Heated Crevice Environments

Topical Report - Results for Mod of Heated Crevice

08/18/1999 - 08/31/2000

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Prepared for:

US Department of Energy
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Attention: Katherine Woo

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Enclosed is the subject report.

Sincerely,
ROCKWELL SCIENCE CENTER, LLC

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Principal Investigator

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AN INVESTIGATION OF THE MECHANISM OF IGA/SCC OF ALLOY 600 IN CORROSION ACCELERATING HEATED CREVICE ENVIRONMENTS

NUCLEAR ENERGY RESEARCH INITIATIVE (NERI) PROGRAM
DE-FG03-99SF21921

Topical Report: Modification of Heated Crevice

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INTRODUCTION

A pressurized water reactor (PWR) steam generator transfers heat from the primary water, heated in the reactor core, to the secondary coolant system. These are shell and tube heat exchangers having the primary water from the reactor inside the tubes and with steam generation on the shell side. This design generates steam on the OD side of the Alloy 600 (or Alloy 690) steam generator tubes, which leads to the concentration of impurities (referred to as hideout) in occluded regions on the tubes. Of major concern is the crevice formed by the tube/tube support plate (T/TSP) intersection. The restricted mass transport in the small crevice volume prevents the species, which concentrate during the generation of steam on the OD of the tube, from quickly dispersing into the bulk water. The presence of a porous magnetite corrosion product from the support plate and deposits, originating from the feed and condenser systems, in the crevice further restricts mass transport, enhancing the concentrating process. This flow restriction leads to the concentration of impurities from the steam generator water by a thermal hydraulic mechanism.

The concentrated solutions in crevices have been a contributing cause of several forms of corrosion of steam generator tubes, including intergranular attack/stress corrosion cracking (IGA/SCC), pitting, and wastage (general corrosion of the tube). The

rate and type of corrosion are dependent on pH, specific anions, and the electrochemical potential (ECP). A key variable is the ECP since the type and kinetics of corrosion processes are determined by the potential.

To control corrosion, plants have increased water purity, reduced oxygen ingress, used buffers such as boric acid, and injected hydrazine to maintain reducing conditions. These measures have been generally successful in controlling all forms of corrosion except IGA/SCC. Tube damage by IGA/SCC continues to result in plant shutdowns due to leakage, extended outages for plugging large numbers of tubes, and replacement of steam generators(1).

The T/TSP crevices are inaccessible during operation of the steam generator; thus, the crevice chemistry must be deduced by indirect means. Modeling by computer codes such as MULTEQ, analysis of corrosion products on the tubes, and analysis of deposits extracted from the crevices have suggested that a caustic solution was present in the crevices when the early cracking incidents occurred(2). Laboratory results, using static autoclaves, have shown that caustic alone can cause IGA/SCC in Alloy 600(3).

The present strategy for mitigating IGA/SCC is based on the assumption that crack initiation and propagation rates depend on pH and the electrochemical potential. Laboratory data(4) using static autoclaves, show that IGA/SCC crack growth rates reach a minimum at pH's between 5 and 9 as shown in Figure 1. The crack growth rates shown in Figure 1 range over an order of magnitude at each pH. The lowest values of crack growth rates for these laboratory measurements were generally obtained when the ECP was lowered by deaeration; the highest values were obtained when the ECP was raised by significant amounts of dissolved oxygen in the test solutions or by applied ECP. Accordingly, all plants have adopted the practice of injecting hydrazine to maintain reducing conditions. Some plants are also adjusting the Na^+/Cl^- ion ratio in the feedwater using a procedure called Molar Ratio Control(5) This procedure is used to control the crevice pH in the range of 5 to 9. These measures have been successful in reducing the rate of increase in tubes affected by IGA/SCC in some plants; however, other plants using the same measures have experienced a rapid increase in IGA/SCC. The reason for this variability is not understood.

Figure 1. EPRI data for SCC rates in alloy 600 versus pH at 315°C (1).

There are several uncertainties in the crevice chemistry control approach used to prevent localized corrosion of tubing in steam generator crevices. The mechanism of IGA/SCC is not understood. It is assumed that pH and ECP are the important variables, but this assumption is based on laboratory data using static autoclaves with what are believed to be simulated crevice chemistries. Much of the laboratory data were generated with no electrochemical control. Moreover, it is assumed that the same cracking mechanisms apply during heat transfer conditions and in static autoclaves. Since steam generator crevices are not accessible during operation, neither the crevice chemistry nor the ECP in the crevice can be measured. Thus, crevice chemistry control methodologies are based on hypothesized relationships between bulk water chemistry and/or calculated results from bulk water chemistry data and hideout return data using computer codes (MULTEQ, Molar Ratio Index, CREV-SIM), which have not been completely benchmarked(5). Moreover, it is assumed that field data

on IGA/SCC correlates with pH although the crevice chemistry is complex containing several species, one of which may be a contributing cause to IGA/SCC.

As an approach to obtaining a better understanding of how crevice chemistries and crevice ECP relate to IGA/SCC steam generator tubes, an instrumented replica of a steam generator T/TSP crevice has been constructed. With the system operating under simulated steam generator conditions, *in situ* measurements can be made of crevice chemistry, electrochemical potential in the crevice, and kinetics of the concentration process. The rate of IGA/SCC is monitored by electrochemical noise. This report describes the heated crevice and its modification for IGA/SCC investigations. A similar system to investigate crevice chemistry has been constructed previously(6).

CONSTRUCTION OF HEATED CREVICE

This key element in the approach is the use of a crevice configuration with the dimensions of a T/TSP steam generator crevice, which is instrumented to monitor the chemistry, electrochemistry, and thermal conditions in the crevice while the tube is pressurized to provide a hoop stress. Figure 2 is a schematic showing the integrated autoclave-heated tube-ring assembly. The assembly consists of an Alloy 600 tube mounted in an Alloy 718 autoclave. A 0.43 mm (17 mil) annular crevice is formed by a 405 stainless steel ring 3.066 cm (1.207 in) long. The tube and ring are structurally independent and mechanically attached to the 1.7 liter autoclave. This type of construction facilitates disassembly and maximizes flexibility. The tube and/or ring can be replaced independently, which permits changes in configuration (asymmetric crevice, broached crevice, packed crevice, closed bottom or open crevice) and replacement of the tube after a SCC test without major reconstruction. All three components are electrically isolated from one another. In initial investigations involving packed crevices, the packing material has been diamond powder. The diamond powder is chemically inert and is an insulating material, assuring that the tube and TSP are electrically isolated from one another.

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Figure 2. Schematic of the heated crevice constructed.

Heat is supplied to the autoclave by strip heaters attached to the sides. The strip heaters can maintain the autoclave at a temperature of 280°C. The Alloy 600 tube is heated electrically by an internal 600W cartridge heater extending 2.5 cm above and below the TSP so that the crevice is uniformly heated. Efficient heat transfer between the cartridge heater and the tube is provided by He gas, which is also used to pressurize the tube. The system is designed so that 40% of the heater filament is adjacent to the crevice. Figure 3 is a photograph of the heater assembly. A copper heater jacket is welded to one end of a thin-wall stainless steel tube, which contains the leads to the heater. A flange is welded to the other end of the tube. The sheaths containing the thermocouple wires from thermocouples at various locations surrounding the heater are brazed at openings in the flange. The white rods in contact with the flange are alumina insulators containing the

thermocouple wires. The thermocouple connectors are visible at the top of the tube.

Figure 3. Cartridge heater assembly.

Figure 4 is an engineering drawing of the tube. The design allows the Alloy 600 steam generator tube to be pressurized to 2700 psi while at simulated PWR steam generator conditions. This provides the stress component for the SCC investigations. The Alloy 600 tube is pressurized through the small tube attached to the side. To the left of the tube, is a drawing of the top of the mini-conflat flange where the cartridge heater assembly is attached. The small tubes surrounding the Alloy 600 steam generator tube and mounted at an angle to the axis of the Alloy 600 tube are feed-throughs for the eight thermocouples which monitor the temperature of the tube wall. These thermocouples are contained in Alloy 600 sheaths and have an OD of 2.5mm. The thermocouples are brazed onto the ID of the tube in a helix arrangement. One thermocouple is located at the top, and one is located at the bottom of the tube. The remaining six are equally spaced in the vertical direction between the top and bottom thermocouples.

Figure 4. The Drawing of the Alloy 600 tube shows the fitting for pressurizing the tube and the thermocouple feed-throughs.

Figure 5 is a photograph of the assembled cartridge heater/tube array. This figure shows the cartridge heater assembly in Figure 3 attached to the tube in Figure 4. The connector at the far right is for power to the cartridge heater. The large thermocouple connectors adjacent to the cartridge heater power connector are for the thermocouples embedded in the copper heater jacket. The remainder of the thermocouple connectors are for thermocouples on the ID of the tube and in the space between the tube and the cartridge heater.

Figure 5. Photograph showing the assembled cartridge heater and Alloy 600 steam generator tube.

Eighteen side ports are symmetrically located around the center section of the autoclave as shown schematically in Figure 6. These ports are used to insert sensors into the bulk solution or through the TSP into the crevice environment. The ports are not located at the same elevation, which allows probes to be inserted into the crevice at different depths. Two ports contain capillary tubes, one for solution extraction from the bulk, and one for solution extraction from the crevice. Solution extraction can be performed while the system is in a normal operating condition. Two ports are used for external Ag/AgCl reference electrodes. One reference electrode is used to monitor the freespan potential. The second reference electrode is inserted through the ring simulating the TSP with the end of the reference electrode capillary terminating in the crevice flush with the inside of the ring. The capillary is constructed of Teflon. Another port is used for the electrochemical noise measurement. Four ports are used to insert Pt and Ni rod electrodes into the bulk and crevice solutions. Each rod is sleeved in Teflon. Teflon has an approximate 10% volume expansion at the 280°C operating temperature, effectively sealing the tube into the opening. A port is also available for inserting the Raman probe. The remaining ports are vacant but can be used for upgrading the system for pH measurements and ac impedance.

Figure 6. A schematic showing the array for sensors in the center ring of the autoclave.

A photograph of the interior of the autoclave with the bottom removed is shown in Figure 7. The six holes visible in the top are for the input and output of the water circuit and for the insertion of sensors into the bulk water. The connectors attached to the seventeen ports for inserting probes into the crevice can be seen surrounding the outside of the autoclave. Figure 8 is a photograph showing the tube and support plate assembly inside the autoclave. Also visible in the photograph are the Teflon sleeved probes extending from the autoclave wall into support plate. The Teflon provides protection from the bulk solution and provides electrical isolation.

Figure 7. Photograph of the interior of the autoclave with the bottom removed.

Figure 8. Photograph of the tube and simulated support plate mounted inside the autoclave.

The assembly drawing of the autoclave is shown in Figure 9. A "clam shell" design is used with the autoclave held together by bolts inserted in clamping rings at the top, bottom and center of the autoclave. Overall dimensions of the system are approximately 25 cm (10 inches) in diameter and 40 cm (16 inches) in length. The heated crevice can be rotated a full 360° for assembly and maintenance. The crevice is located in the center of the autoclave:

Figure 9. An assembly drawing of the heated crevice with inserted steam generator tube.

Figure 10 is a photograph of the assembled heated crevice. The radial array of ports for sensors can be seen surrounding the center section of the autoclave. An Alloy 600 tube, which does not have the heater assembly attached, is clearly visible in the center of the top section of the autoclave. There are six feedthroughs located in the top of the autoclave. These are for the water system and for inserting probes and thermocouples into the bulk water. Stainless steel rods, inserted into the center clamping ring, support the heated crevice on a stand so that it is suspended above the floor.

Figure 10. Assembled heated crevice.

Figure 11 is a photograph showing the complete layout. The autoclave containing the crevice is in the center of the photograph. Compressed He, in the cylinder to the left of the autoclave, is used to pressurize the tube. Distilled water is delivered to a mixed resin bed (not shown) where it is freed of ionic contamination up to 18 megohm-centimeter. A high pressure pump pumps deoxygenated water from the feed tank (located at the far left in the photograph) through the remainder of the water circuit. Before entering the autoclave, the water passes through a preheater. Water exits the system after passing through a condenser. A backpressure regulator in front of the condenser allows the pressure in the autoclave to be adjusted for a boiling point of 280°C . The panel on the wall at the far right contains the circuits and controls for the band heaters on the autoclave and the tube heater.

Figure 11. Complete set-up showing the heated crevice, the water circuit, and the control panel.

Data Acquisition Unit

A Pentium II computer with National Instruments Labview 5.1, Keithley 7001 Scanner/Switch, 2000 Digital Multimeter, and 6512 Electrometer controls the Data Acquisition System (DAS). The 7001 has a 39 channel #7014 T/C card in slot #1 and a 10 channel #7158 Low Current Scanner card in slot #2. The #7014 card converts the microvolt signals from the Type K thermocouples to temperatures. The #7158 reads the millivolt signals from the two silver/silver chloride electrochemical reference electrodes and the metal rod electrode references which extend into the crevice and the bulk solution. The recorded data is the average of ten readings. Seventeen seconds are required for the DAS to collect a complete set of data from all of the thermocouples and the electrodes. All instruments and the computer for the DAS are mounted in a 19 inch wide rack. The frequency of data collection is pre-selected and can be changed at any time during a run. The temperatures and ECPs of

the reference electrodes are displayed continuously on the monitor and are updated during each data collection sequence.

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