# 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

## TECHNICAL PROGRESS REPORT

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This program focuses on understanding mechanisms causing corrosion damage to steam generator tubes in a pressurized water reactor (PWR). The crevice formed by the tube/tube support plate (T/TSP) intersection in a PWR steam generator is a concentration site for nonvolatile impurities (referred to as hideout) in the steam generator water. The restricted mass transport in the small crevice volume prevents the species, which concentrate during the generation of steam, from quickly dispersing into the bulk water. 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.

Damage to Alloy 600 steam generator tubes by IGA/SCC continues despite rigorous water chemistry controls during power operation. The continued degradation has resulted in operational leakage, extensive tube inspections and repair. Eventually, replacement of steam generators or plant decommissioning must be considered. Many remedial actions against IGA/SCC have been taken, which include: increases in secondary water purity, reductions in oxygen ingress, use of buffers such as boric acid, injecting of hydrazine to maintain reducing conditions, and control of molar ratios of cations and anions. These measures have been useful in reducing the rate of increase in tubes affected by IGA/SCC

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in some plants; however, other plants using the same measures have continued to experience IGA/SCC.

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 (ECP). Laboratory data, using static autoclaves, show that IGA/SCC crack growth rates reach a minimum at pH's between 5 and 9 under electrochemically reducing conditions. Some plants are injecting Na and Cl ions into the feedwater to adjust the crevice pH. There are several uncertainties in this approach. Since measurements of crevice chemistry and electrochemical potential (ECP) cannot be made in an operating steam generator, estimates are made using computer codes based on hypothesized processes believed to occur in crevices. Moreover, laboratory IGA/SCC data were obtained in static autoclaves using simulated crevice solutions. The IGA/SCC mechanism may be different under heat flux conditions, during which steam is being generated. Crevice chemistries are complex and pH may not be the important factor or the only important factor.

The objective of this program is to develop an understanding of the corrosion accelerating mechanisms, particularly IGA/SCC, in steam generator crevices. The important variables will be identified, including the relationship between bulk water chemistry and corrosion accelerating chemistries in a crevice. The approach will use an instrumented heated crevice, which is a replica of a PWR steam generator tube/TSP crevice. With the system operating at simulated steam generator thermal conditions, measurements can be made of the chemical, electrochemical, and thermal conditions in the crevice. Damage to the tube due to IGA/SCC and other corrosion processes will be monitored using electrochemical noise.

Task 1: Modification of Heated Crevice for SCC and Electrochemical Noise Measurements.

1. Task Status.

The design of the system has been completed and construction is underway on schedule. Figure 1 is a drawing showing a cross sectional view of the heated crevice and shows only the portion of the steam generator tube, which is inside the autoclave. The heated crevice is constructed so that the autoclave, the ring, simulating the

TSP, and heated tube are structurally independent. All three components are electrically isolated from one another. The tube and ring are mechanically attached to the 1.7liter autoclave. This allows easy disassembly so that the tube can be removed for analysis and replacement after SCC has been induced. The system is designed to incorporate sensors to monitor the crevice environment. The sensors are inserted into the crevice through openings in the side of the simulated TSP. Each sensor is cocooned in a Teflon sleeved Alloy 600 tube. The Teflon has a 10% volume at 280°C operating temperature, effectively sealing the tube into the opening. These openings are located so that sensors can be inserted at different elevations in the crevice, as shown in Figure 1. Electrochemical potential measurements are made with external Ag/AgCl reference electrodes located in the crevice and in the bulk solution. Solution extraction is performed from the autoclave water and from the crevice through capillary tubes while the system is fully operational. The capillary tubes also permit solutions to be injected into the crevice during operation.

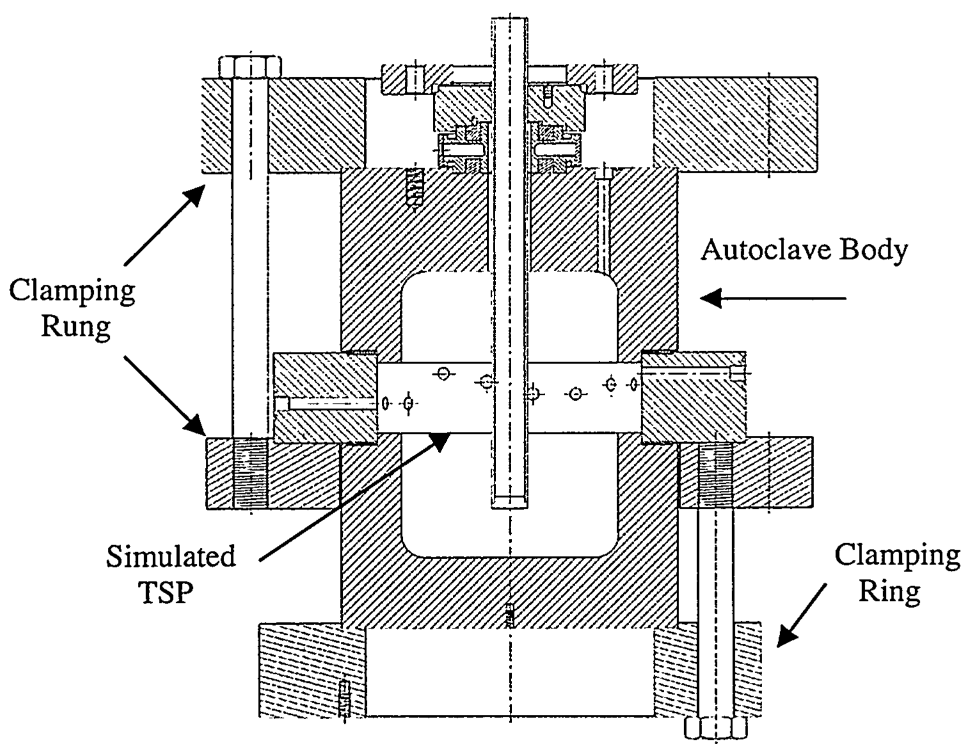



Figure 1. Schematic of the heated crevice with inserted steam generator tube.

Figure 2 is a 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. An internal electric cartridge heater provides heat, simulating the primary water. Eight thermocouples are brazed on the ID of the tube at different elevations within the crevice. The whole assembly is electrically isolated from the Alloy 600 ring, simulating the TSP, forming a crevice 2.5 cm long and having a 0.3 mm gap. Figure 2 shows the high pressure fitting for pressurizing the tube, the feed throughs for the thermocouple leads and the flange for attaching the tube assembly to the autoclave. A tube has been completed and successfully tested. Figure 3 is a photograph of the completed tube.

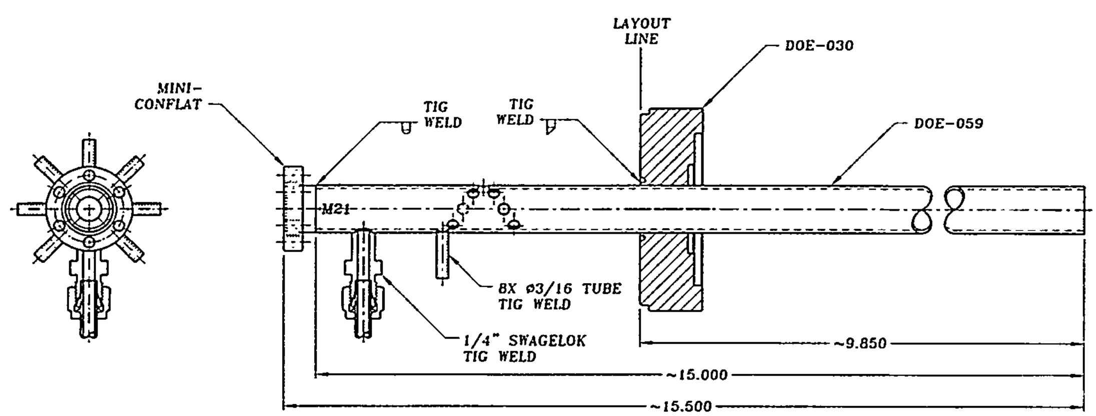



Figure 2. The Drawing the Alloy 600 tube showing the high pressure fitting and the thermocouple feed throughs.

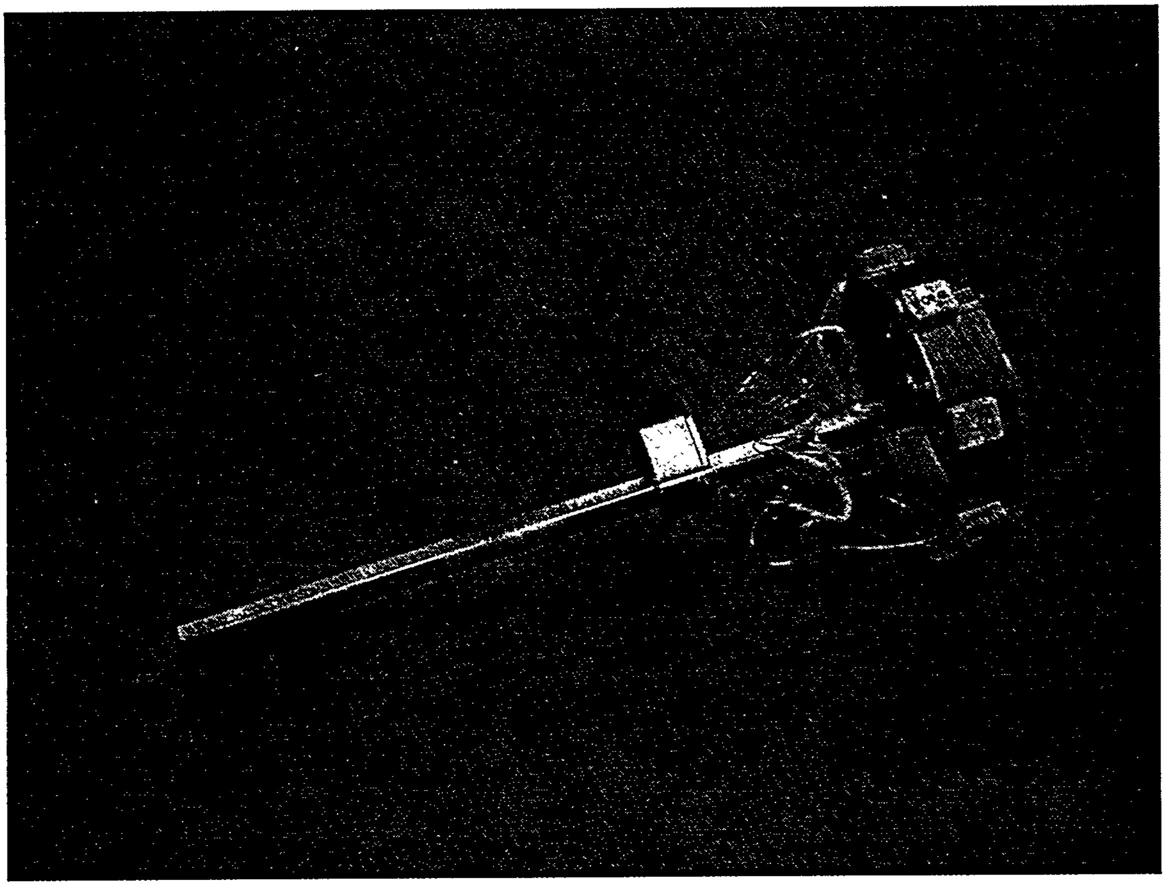


Figure 3. Photograph of the Alloy 600 steam generator tube ready for assembly into the heated crevice.

2. Issues/Concerns.
None

Task 2: Evaluation of Electrochemical Noise

1. Task Status.

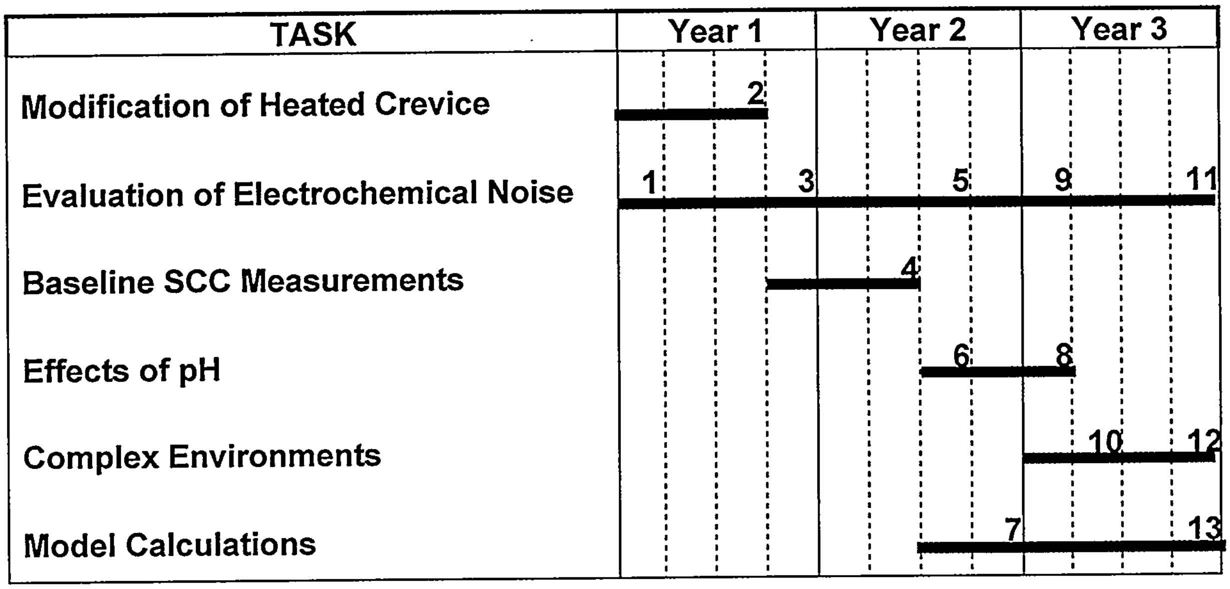
All electrochemical noise analysis (ENA) investigations of the various corrosion processes, including SCC, employ the same basic setup and analysis of results. For the typical ENA experiment two electrodes are coupled together via a zero-resistance-ammeter (ZRA), and the potential of the couple is monitored with respect to either a reference electrode, or a pseudo reference electrode. The time records for the current and potential allow evaluation of a number of statistical parameters for the respective signals such as the standard deviation of the voltage noise, $\sigma_v$, or current noise, $\sigma_c$, the ratio of which defines the noise resistance $R_n = \sigma_v / \sigma_c$. The noise resistance is a parameter used to monitor the kinetics of DC and other corrosion processes. The electrochemical noise during SCC will be collected with the pressurized tube coupled to the simulated TSP via a zero resistance ammeter. The potential of this couple will be monitored with respect to the crevice reference electrode. Previous work has found that analysis of the noise data give the onset of crack initiation and the kinetics of crack propagation.

The hardware and software for electrochemical noise analysis ENA have been tested successfully for a simple corroding system at room temperature. The current and potential noise have been collected and analyzed to calculate $R_n$ and other statistical parameters. This has provided a system validation of the instrumentation and methodology to be used in the heated crevice work. We are now ready to monitor and analyze electrochemical noise during SCC in the Alloy 600 steam generator tube on the completion of Task 1.

2. Issues/concerns

   None

## MILESTONES




1. Complete design of electromechanical noise sensor. **(Completed)**

2. Complete construction of heated crevice for IGA/SCC and electrochemical noise measurements. **(Initiated)**

3. Complete initial evaluation of SCC by electrochemical noise. **(Initiated)**

4. Complete IGA/SCC reference measurements.

5. Complete analysis of electrochemical noise from reference conditions.

6. Complete IGA/SCC measurements in alkaline conditions.

7. Compare laboratory results with model calculations for alkaline conditions.

8. Evaluate effects of pH on IGA/SCC.

9. Evaluate pH effects on IGA/SCC initiation and propagation mechanism by electrochemical noise.

10. Make IGA/SCC measurements in hydrazine chemistries.

11. Evaluate affects of complex environments on IGA/SCC mechanism using electrochemical noise.

12. Determine if pH alone or other complex chemical variables control IGA/SCC.

13. Benchmark models for crevice chemistry and IGA/SCC.