On-Line Monitoring of SG Crevice Chemistry Evolution

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In a locally restricted steam generator (SG) geometry, impurities in the bulk water can be concentrated by boiling process to extreme pH that may then accelerate the corrosion of tubing and adjacent materials. To mitigate the corrosion, the molar ratio control technique is widely implemented with the EPRI initiative. In order to maximize its beneficial effect, understanding of crevice processes needs to be advanced. To simulate a real SG tubesheet crevice high temperature/high pressure crevice simulation system has been developed. Primary water with high flow rate flowed through the 3/4" outer-diameter tube and crevice section was made at the outside of the tube. The simulation apparatus was equipped with thermocouples and electrodes for the measurement of temperature and electrochemical corrosion potential (ECP) in the crevice and free span respectively. Secondary solution composed of 50 ppm Na and 196 ppb H_2 was supplied with the flow rate of about 4 L/hr. In an open tubesheet crevice with 0.15 mm gap and 40 mm depth, axial temperature profile and ECP were measured as a function of time and available superheat. NaOH concentration process in crevice was confirmed from temperature and ECP data. Experimental data showed a similar behavior to calculated results by a thermodynamic equilibrium code.
From the boiling point elevation data, maximum crevice concentration factor was estimated as about 500 for $\Delta T=20$ ℃ and about 1000 for $\Delta T=25$ ℃. To simulate fouling crevice with sludge or impurities, magnetite-packed crevice experiment was conducted. In the same condition, packed crevice has much longer time constant for Na concentration and showed heavier concentration than open crevice.

Keywords : *steam generator, tubesheet crevice, boiling point elevation, electrochemical corrosion potential*

1. Introduction

In a pressurized water reactor (PWR), SG tubes are made of alloy 600 or 690 and steam is produced on the outer diameter side of the tubes. The SG reliability has been one of the important issues encountered during the PWR operation. Various corrosion phenomena in the SG were observed in the past.[1] In a locally restricted SG geometry, trace impurities in the bulk water can be concentrated by boiling processes to extreme pH. SG tube degradation phenomena result from the concentration of impurities mainly in three locations in the SG: the tube support plate crevice, the tubesheet crevice, and the sludge pile. These locations with concentrated solutions may then develop outer diameter stress corrosion cracking/intergranular attack (ODSCC/IGA), which is the one of the principal degradation mechanisms in recent years.[1] To mitigate the ODSCC/IGA in the restricted geometry and to maintain SG tube reliability, the detailed understanding of boiling crevice phenomena is necessary.

A near-neutral crevice is the environment likely to produce the lowest SCC/IGA crack growth rate.[2] Based on this fact, the Electric Power Research Institute (EPRI) has developed the molar ratio control (MRC) program, of which the goal is to maintain the crevice pH nominally in the range between 5 and 9 at the operating condition.[3] But, within plant operation, no one knows the crevice conditions. Therefore real-time crevice monitoring methods need to be developed.

Baum[4] reviewed, in detail, the thermal-hydraulic and chemical phenomena in restricted regions and the free span area. Early studies about crevice experiment were primarily focused on the characterization of thermal-hydraulic nature. Chemical concentration and chemical or electrochemical measurement in a crevice were studied more recently. Kozawa and Aoki[5] investigated experimentally several characteristics of boiling in a crevice between tube and tubesheet. A flat crevice and a fluid heating method were adopted. Experimental results showed that three kinds of boiling configurations could occur in a crevice.

Baum and Curlee[6] performed tests, which simulated the geometric, thermal, and hydraulic environment found between the tube and the TSP in typical PWR U-tube SGs. It was found that certain tube support configurations could produce a local liquid deficient heat transfer regime, which, in turn, could permit significant chemical concentration. The interrelationship between the heat and the mass transfer processes in the confined geometry was further demonstrated by comparing the results of an analytic model. Sodium hideout studies in SG crevices were carried out systematically by Campan and Shoemaker.[7] A method using Na^{24} as a tracer was developed.

A technique was developed to study electrochemical phenomena in crevices that simulate the geometry in nuclear SGs by Hermer et al.[8] Electrochemical potentials were measured in TSP crevice geometry. Lumsden et al.[9] constructed a system, which operates with simulated SG crevice thermal conditions. The results obtained for the average boiling point elevation in the crevice, the analysis of the extracted crevice solutions, and the redox potential in the crevice and free span, after equilibrium was attained, agreed well with MULTEQ® predictions. The electrochemical noise monitoring technique was evaluated in a refreshed autoclave system for eventual corrosion monitoring system in SGs.[10]

An on-site model boiler facility was constructed in the Kansai Electric Power Company OHI Unit 1 at beginning of 1986.[11] Corrosion potential monitoring in the bulk secondary water and pH monitoring in simulated SG crevices were carried out using the model boiler.[11] By analyzing directly sampled concentrated solution from heated crevice of an on-site autoclave, SG crevice environment was evaluated.[12),13]

Based on earlier work, the objectives of this study are to directly observe the crevice phenomena at high temperature/high pressure (HT/HP) and to measure chemical, thermal-hydraulic, and electrochemical parameters in a boiling crevice. Single-ended crevice was designed to represent a tubesheet crevice.

2. Experimental

In the earlier works of the authors, electric heater was used to simulate primary heating condition. But the heating method by electric heater caused such problems as the non-uniformity of surface heat flux and difficulty in simulating real SG temperature distribution. Therefore, to simulate a real SG tubesheet crevice HT/HP crevice simulation system has been developed. The system is composed of two main parts: primary water flow loop and secondary water flow loop. Primary water with high flow rate of about 2300 L/hr was circulated by HT/HP circulation pump through the 3/4" outer diameter (OD) 316 stainless steel (SS) tube. 1-gallon autoclave was used as the primary heater of which maximum power was 4.8 kW. High purity water purged with 5% hydrogen gas (Nitrogen bal.) was charged by high pressure pump and ejected by back pressure regulator. Primary pressure was maintained at 2050 ± 30 psig.

In Fig. 1, SG simulation vessel is schematically described. The vessel was made of 316 SS. To protect vessel failure by caustic stress corrosion cracking, electroless Ni plating with 10 μm thickness was applied on the whole vessel surface. Secondary water composed of 50 ppm Na and 0.196 ppm H_2 was charged by high pressure pump and ejected by back pressure regulator. Also, secondary water storage tank made of Ti was purged with 5% hydrogen gas (Nitrogen bal.) to remove oxygen. The flow rate of secondary system determined by the charging rate of high pressure pump maintained the value of 4 L/hr. Secondary pressure was adjusted automatically by PID controlled pressure regulator and maintained at 790 ± 5 psig of which equivalent saturation temperature was 270 oC. The secondary solution composed of 50 ppm sodium and 0.196 ppm hydrogen was used. As described in Fig. 1, to make bottom-closed crevice the electrolytic Ni plating was applied on the crevice section of the 3/4" OD SS tube, and the plated section was machined as the required dimension.

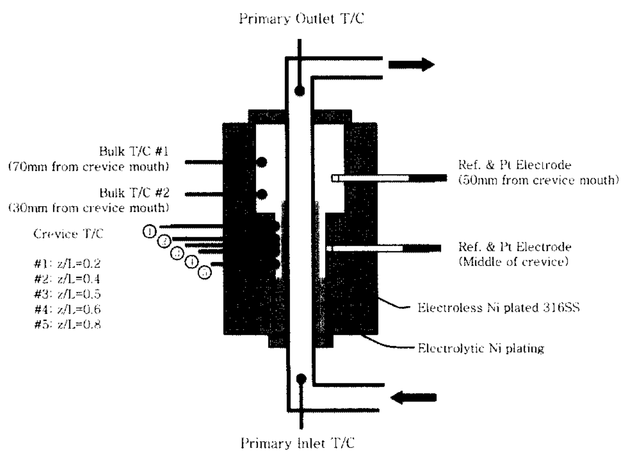

Fig. 1. The schematic diagram of the SG tubesheet crevice simulation vessel.

The SG tubesheet crevice simulation vessel was equipped with thermocouples and electrodes for the measurement of temperature and ECP in crevice and bulk water. Fig. 1 shows the location of sensors installed in crevice and bulk region. Two thermocouples were installed at bulk region and five thermocouples were installed at crevice region. Also, primary inlet and outlet temperatures were monitored. Ag/AgCl (Water) electrode of which filling solution was high purity water was used as reference electrode and two Pt electrodes were installed. Before the experiments, Ag/AgCl (Water) electrodes were calibrated as a function of temperature. In both crevice and bulk region, reference and Pt electrode had the same axial location. In a tubesheet crevice with 0.15 mm gap and 40 mm depth, axial temperature distribution and Pt potential vs. Ag/AgCl (Water) were measured with time. Under the assumption that Ni electrode would be served as hydrogen electrode in reducing environment, the autoclave body potential vs. Ag/AgCl (Water) was also measured. The voltage was measured by HP 34401A multimeter through the HP 3495A scanner.

3. Results and discussion

3.1 Open crevice test

Fig. 2 shows the axial temperature profiles with variation of primary water temperature. The vertical axis means the normalized level with the crevice depth and zero means the level of a crevice mouth and positive value means the upper region of the crevice. As the difference between the primary temperature and secondary saturation temperature, ΔT increased, the temperature gradient in crevice increased and the temperature in all positions even with bulk region shifted to higher temperature direction. In case that the primary temperature equals to 300 ℃, the temperature of bulk region exceeds the saturation temperature. It means that the secondary water flow rate is not enough to maintain subcooled condition. Fig. 3 shows the temperature variation results as a function of time at the condition of ΔT=25 ℃. Secondary pressure maintained the value exceeding the saturation pressure corresponding to the primary temperature until the primary temperature became stable. And then, the pressure was suddenly dropped to 790 psig and boiling in crevice occurred. As shown in Fig. 3, the temperature reached the stationary state about 10 hours later after boiling occurred. As described in Fig. 1, 'TC#1' represents the shallowest position and 'TC#5 represents the deepest position. It is found that from the shape of temperature variation the crevice region is divided into two regions. One is the region including 'TC#1', 'TC#2', and 'TC#3'

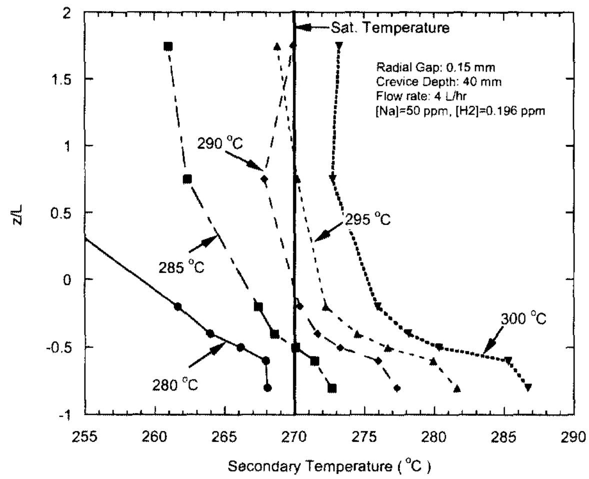

Fig. 2. The axial temperature profiles with variation of primary water temperature at the condition of open tubesheet crevice.

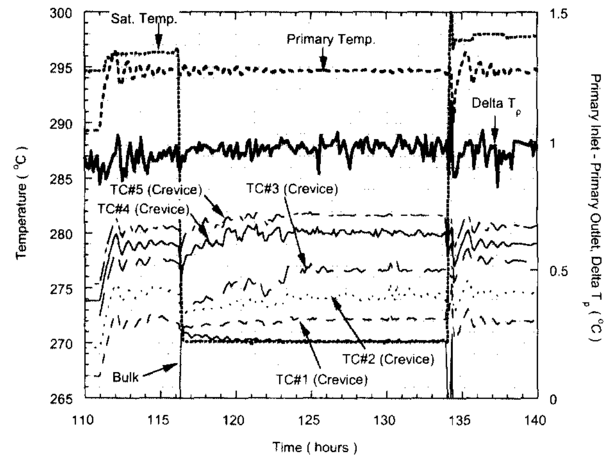

Fig. 3. The temperature variation results as a function of time at the conditions of open crevice and ΔT=25 ℃.

and the other is the region including 'TC#4' and 'TC#5'. Based on the earlier works,[5),6)] it is concluded that the former region represents the wet and/or wet and dry region and the latter the dryout region. It means that liquid can penetrate only to the former region. The difference between the primary inlet temperature and the outlet temperature, ΔT_p also was shown but there was no significant change. When the boiling was suppressed by increasing the pressure, the temperature moved to the initial value.

Fig. 4 shows the temperature and potential variation results as a function of time at the same condition as Fig. 3. Before boiling the bulk and crevice ECP maintained the values of about -800 mV_{SHE}. After boiling, bulk ECP slightly decreased and crevice ECP showed fluctuation. Crevice ECP suddenly dropped and remained stable at -920 mV_{SHE}. It means that the crevice solution concen

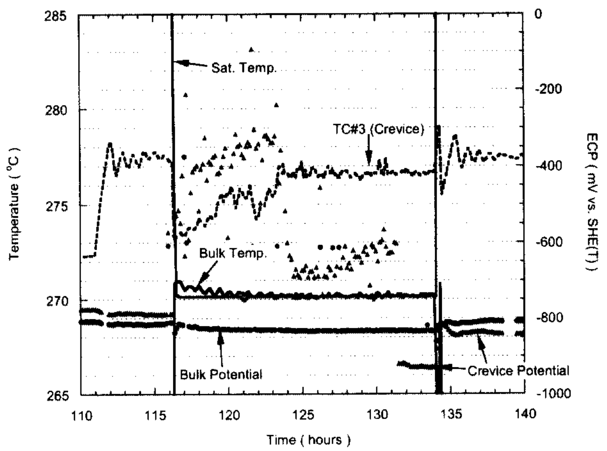

Fig. 4. The temperature and potential variation results as a function of time at the conditions of open crevice and $\Delta T=25$ ℃.

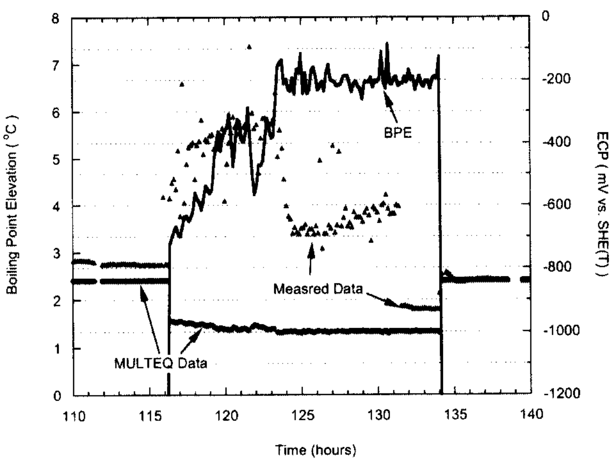

Fig. 5. The measured potential results in comparison to the MULTEQ predicted results at the conditions of open crevice and $\Delta T=25$ ℃.

trated by boiling process leads to the increase of solution pH, which causes ECP decrease. When the boiling was suppressed, crevice ECP did not return to the initial value differed by about 40 mV. 'TC#3 (crevice)' represents the temperature located at the same level as Ag/AgCl (Water) electrode.

By using MULTEQ-REDOX® Ver.2.22 high temperature solution pH, boiling point elevation, and oxidation reduction potential (ORP) were calculated.[14] System temperature was set to be 270 ℃ and flowing option was used. In Fig. 5, the measured potential results were compared with the MULTEQ® calculated results. Experimental data showed a similar behavior compared with calculated results by MULTEQ® although the absolute values showed some discrepancy.

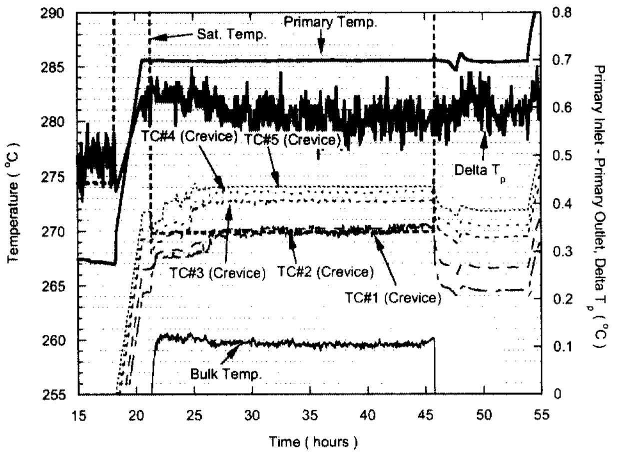

Fig. 6. The temperature variation results as a function of time at the conditions of packed crevice and $\Delta T=15$ ℃.

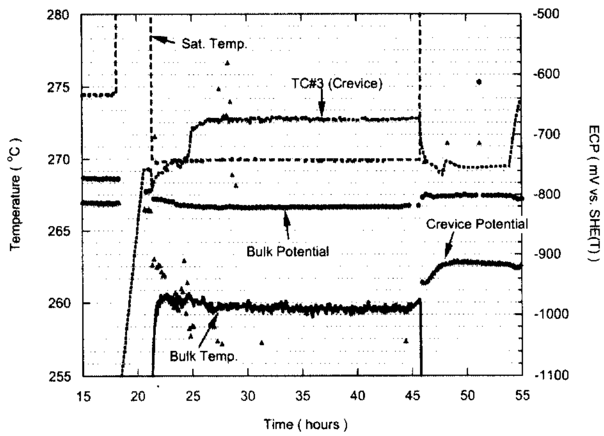

Fig. 7. The temperature and potential variation results as a function of time at the conditions of packed crevice and $\Delta T=15$ ℃.

From the boiling point elevation data, 0.15 mm open tubesheet crevice concentration factor was estimated as about 1000 for $\Delta T=25$ ℃ in the case of 50 ppm Na solution.

3.2 Packed crevice test

To simulate fouling crevice with sludge or impurities, magnetite-packed crevice experiment was conducted. The porosity in the packed crevice could not be measured. Fig. 6 shows the temperature variation results as a function of time at the condition of $\Delta T=15$ ℃. In this case, the region including 'TC#3', 'TC#4', and 'TC#5' can be designated as wet and dry region where concentration takes place well. The region including 'TC#1' and 'TC#2' is under non-boiling condition. As shown in Fig. 6, the temperature reached the stationary state about 7 hours later after boiling occurred. ΔT_p also was shown but there was no significant change. When the boiling was suppressed by increasing the pressure, the temperature returned to the initial value.

Fig. 7 shows the temperature and potential variation results as a function of time at the same condition as Fig. 6. Bulk ECP shows very stable behavior and the ECP in boiling condition is slightly lower than the ECP in non-boiling condition. This is probably because the temperature of bulk solution increases when boiling occurs. Crevice ECP maintained the values of about -820 mV_{SHE} before boiling. After boiling, crevice ECP decreased with some fluctuation but the ECP could not be measured due to the missing of electric path by boiling. When the boiling was suppressed, crevice ECP showed the value of -950 mV_{SHE} and ECP increased gradually but did not returned to the initial value. It seems that under the packed crevice condition the mass transport is restricted and some of the sodium ions concentrated by boiling process diffuses out but some remains in crevice. The difference between the initial crevice ECP and the ECP shortly after increasing pressure is 130 mV. MULTEQ® calculated results using the boiling point elevation data is about 120 mV and shows a good agreement with the experimental results.

Fig. 8 shows the axial temperature profiles with variation of primary water temperature at the condition of packed crevice compared with the case of open crevice. Except the case of 280 ℃, the temperature in crevice region for the packed crevice is about 2 ℃ higher than the one for the open crevice. In the case of 280 ℃, the temperature at shallow crevice is higher than deep crevice. It may be the effect of the packed condition but is not clear. In the same condition, packed crevice has much longer time constant for Na concentration and showed heavier concentration than open crevice.

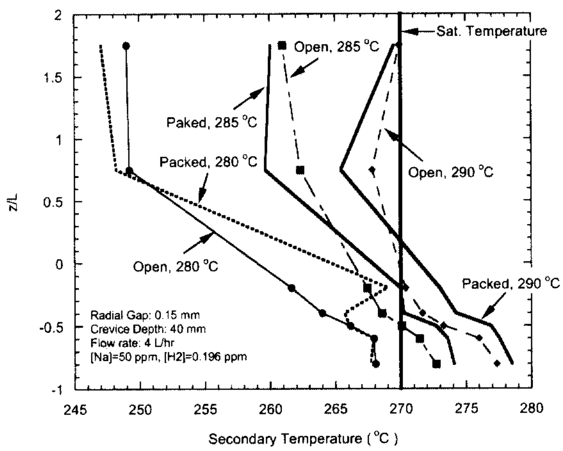

Fig. 8. The axial temperature profiles with variation of primary water temperature at the condition of packed tubesheet crevice compared with the case of open tubesheet crevice.

4. Conclusions

1) Na concentration process in an open tubesheet crevice was confirmed from the temperature and potential measurement data.

2) From the boiling point elevation data, 0.15 mm open tubesheet crevice concentration factor was estimated as about 1000 for ΔT=25 ℃ in the case of 50 ppm Na solution. As ΔT increased, the temperature gradient in crevice and time constant for concentration increased.

3) To simulate fouling crevice with sludge or impurities, magnetite-packed crevice experiment was conducted. In the same condition, packed crevice has much longer time constant for Na concentration and showed heavier concentration than open crevice.

4) By using MULTEQ-REDOX® Ver.2.22 high temperature solution pH, boiling point elevation, and ORP were calculated. Experimental results for both open and packed crevice showed similar behaviors compared with calculated results by MULTEQ®.

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