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Experimental Simulation of Boiling Crevice Chemistry

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Abstract

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 (MRC) technique is widely implemented with the EPRI initiative. In order to maximize its beneficial effect, the understanding of crevice processes need to be advanced. For direct observation of the processes, low temperature simulation experiments have been conducted for both tubular and planar crevices with transparent windows in a dilute NaOH solution at atmospheric pressure. The simulation apparatus is also equipped with thermocouples and microelectrodes for the measurement of temperature and pH. NaOH crystallization were observed in similar patterns reported in earlier studies. The boiling crevice was divided into three regions: wet, dry and wet, and dry region. In both tubular and planar experiments, the magnitude of heat flux and the gap size are found to be important factors governing the concentration kinetics.

1. Introduction

In the Pressurized Water Reactor (PWR), SG tubes were 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 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/Inter-Granular 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 IGA/SCC crack growth rates [2]. Based on this facts, 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 to 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 ultimate goal of this study are to generate the basic data for High Temperature/High Pressure(HT/HP) crevice simulation system development. The objectives of this study at first step are to directly observe the crevice phenomena at low temperature and to measure chemical, thermohydraulic, and electrochemical parameters in boiling crevice. It is also included to determine design parameters for HT/HP crevice simulator. Various crevice configurations including single-ended tubular and planar geometry without packed materials are studied. Single-ended crevices were designed to represent a tubesheet crevice.

2. Experimental

2.1 Tubular Crevice

A 21.4 mm OD 304 stainless steel (SS) tube(thickness: 1.2 mm) was inserted into a 22 mm ID Pyrex tube into making a 0.3 mm gap tubular crevice. Polytetrafluoroethylene (PTFE) tape was wrapped around the SS tube to make a closed-bottom and leak-tight crevice. Inside the SS tube a 400 W electric heater was placed, and a copper insert was introduced to fill a gap between the tube and the heater and enhance thermal conduction. PTFE block supported the tubular crevice structure and this structure was placed in a 1 L Pyrex glass cell. The 1 L cell was put on a hot plate/stirrer. Fig. 1 describes the experimental apparatus of the tubular crevice experiment.

The SS tube surface was mechanically polished with #1200 SiC paper and #1500 paper in sequence to have uniform surface roughness. The crevice has nominally 0.3 mm gap width and 30 mm depth. Due to technical difficulty, the final tubular crevice is found to be eccentric. Resultant crevice gap was about between 0.2 and 0.4 mm and heated length of the SS tube was 50 mm. A 200 ppm NaOH solution was used as bulk water, and the bulk water was stirred. To simulate the SG water condition, deaeration condition was achieved by bubbling pre-purified nitrogen gas through the bulk water. The gas bubbling was continued throughout the experiments. The atmospheric and static condition was maintained for the bulk solution. The internal heater was powered by a thyrister power regulator (TPR) and a PID controller. Direct observation for the boiling crevice through the glass cell was made periodically.

2.2 Planar Crevice

For in situ crevice pH measurement, a tungsten electrode and an Ag/AgCl

(0.1 M KCl) electrode were used. An 1/8" OD tungsten rod with thinned tip was prepared. Heating in air for 7 to 8 min using a propane gas torch oxidized the rod. The rod was then coated with heat-shrinkable PTFE, leaving the exposed tip. For measurement of pH in aqueous solutions at high temperature, membrane electrodes, metal-metal oxide electrodes, or hydrogen electrode can be used [14]. Tungsten electrode for pH measurement at high temperature was introduced successfully by Kirksunov and Macdonald [15]. Also, buffered tungsten electrode was used as reference electrode at low temperature [16] and high temperature [17]. Fig. 2 shows the potential of tungsten electrode at room temperature. The deviation of the slope (-45 mV/pH) from the 59 mV/pH Nernstian slope indicates that tungsten does not respond to pH in a thermodynamically reversible fashion [16]. Also, in ref. 22 it is stated that Eq. (1) can be used to calculate the potential of the tungsten electrode relative to the saturated calomel electrode (SCE) at room temperature.

$$E = -44.3pH + 53.3 \tag{1}$$

where E is the potential of tungsten electrode vs. SCE in mV.

The Ag/AgCl electrode has been used as a reference electrode at high temperature for many years [18-20]. The procedure of making the electrode was referenced by other work [21].

An inner square channel made of 304 SS was surrounded by an outer square structure for making planar crevices. Fig. 3 describes section view of planar crevice parts. 0.1, 0.3, 0.5, and 1.0 mm crevice was machined at each side respectively. For direct observation, glass windows were mounted. Also, instrumentation hole was machined through the window for pH and crevice solution temperature measurements. The SS channel surface was mechanically polished with #800 SiC paper and #1000 paper in sequence to have uniform surface roughness. An 1 kW electric heater with a square cross-section (30× 30×100 mm) was installed in the same way as in the tubular crevice experiment. Four thermocouples were embedded in each square channel surface and measured temperature profile at planar crevice surfaces. Fig. 4 shows the schematic of the experimental apparatus for planar crevice experiment. The overall system has the recirculation system of the 200 ppm NaOH solution. For recirculation, a diaphragm-type metering pump of which maximum charging rate was 60 mL/min was used. All parts contacting solution were made of PTFE or ceramic and chemical contamination was avoided. Bulk solution tank having 89.1 mm OD was made of 304 SS and bolt-connected with under-crevice sections. The solution tank was thermally insulated by ceramic fiber. The solution level in the tank was maintained 400 mm above from the top of crevices. Flooding solution were pumped into a 1 L Pyrex cell. All 1/4" tubing for handling the solution were made of PTFE.

A 200 ppm NaOH solution in the Pyrex cell was heated up to 70 ℃. Then, the solution was transferred to the bulk solution tank by the metering pump. The solution in the Pyrex cell was maintained at 80~90 ℃ in aerated condition throughout the experiment. The deaerated condition was not achieved due to the gas leak problem. The depth and length of heated crevice was 40 mm and 100 mm. Heating power was controlled by TPR and PID temperature controller. Thermocouple outputs were multiplexed by an isothermal scanner, HP3495A, and compensated with an electronic cold junction. The voltage was measured by HP34401A digital multimeter through the scanner.

3. Results and Discussion

3.1 Tubular Crevice

A test was performed for 8 days at 100 ℃ of bulk temperature and heat flux of about 33 kW/㎡. After about 5 hours, sodium hydroxide precipitation started to appear at the interface between wet region and dry region as described in Fig. 5. Due to the eccentricity of crevice, the concentration phenomena were varied circumferentially to peak in the region of narrowest gap. As the time increased, the precipitation region spread both in circumferential and vertical directions and preexisting precipitates became denser. After 4 days, there was no further change in the appearance of the precipitation region. Precipitates in the crevice did not dissolve back in the bulk when the heaters were turned off.

In this experiment, crevice boiling regions are divided into three regions: liquid penetration & discharge (or wet) region, liquid drop scattering (or dry & wet) region, and dryout region. Earlier work described the tubesheet crevice as the mixture of boiling regimes [5]. Similar results were observed in this experiment. Fig. 5 (a) shows the liquid penetration, liquid drop scattering, and dryout in the tubesheet crevice. At the location having the larger crevice gap size, water penetrated to the bottom of the crevice, and hence the mixing with bulk solution occurred more actively without any precipitation.

Baum [6] found that local liquid deficient heat transfer regime (dry & wet or dryout region) produced significant chemical concentration. Results of this experiment confirmed the Baum's results as shown in Fig. 5 (b). Fig. 5 (b) shows the crystallization pattern at the most narrow gap side in the tubesheet crevice. Semi-circular precipitate region is divided into two areas: the inner circular dryout region and the outer circular dry and wet region. It is shown that NaOH precipitates can take place at heat flux that is below the value for SG hot-leg tubesheet.

As sodium hydroxide is nearly insoluble in vapor phase, sodium hydroxide remains in liquid phase. If the liquid is occluded and not mixed with bulk solution, such as at the bottom of crevice, concentration process occurs and can lead to precipitation. At the top region of the tubesheet crevice, liquid penetration and discharge is repeated, and concentration process does not occur. But solution is not mixed at the bottom region of the tubesheet crevice. Sodium hydroxide just remains and concentrates.

As shown in Fig. 6, the observed penetration depth of water is greater than the prediction by an existing model [22]. The model can be derived from Wallis correlation. At the narrowest side in the crevice liquid penetration depth was about one half of full depth, 30 mm. Because liquid penetrated into the bottom of crevice at the opposite side, liquid penetration depth would be more than 30 mm. The tendency of penetration depth increase with the gap width is in agreement with the prediction.

3.2 Planar Crevice

Temperature profiles in the top-open planar crevices were monitored. Fig. 7 shows the temperature history for the crevice of 0.3 mm gap. The control temperature of inner Cu insert was raised stepwise. In Fig. 7, the cause of bulk water oscillation appears to be the stepwise increase of heat flux. The oscillation is more stabilized during the final steady operation at the highest heat flux. The initial temperature difference between positions was small, but as heat flux rose, the temperature difference also increased. The bulk temperature transients at 110,000 sec and 220,000 sec were caused by a metering pump failure and a leak in recirculating steam-line joints, respectively. At the most of time, the surface temperature increased with increasing depth into the crevice. The thermocouple #4 in Fig. 7 shows that the scattering of the temperature became broader and increased slowly at the highest heat flux region. But it seems that the boiling regime is not changed from wet condition into dry and wet condition. In constant heat flux experiment, there is no transition, such as that from a steam blanketed state to a fully wetted state. Initially steam blanketed region in crevice always remained dry condition.

Fig. 8 shows the potential of tungsten electrode vs. Ag/AgCl (0.1 M KCl) reference electrode and the crevice surface temperature histories. The potential signal was an unexpected value. Due to the active boiling in crevice, the electric path could not be formed, and hence this odd signal was generated.

4. Conclusion

Tubular crevice experiment, without detailed instrumentation, provided useful insight on crevice phenomena. Results consistent with those of Baum's were obtained as to the chemical concentration phenomena. In crevice boiling configuration, the gap size and heat flux are observed to be the most important factors. It is demonstrated that NaOH crystallization can occur in a tubesheet crevice at relatively low heat flux values. It is confirmed that precipitation occurs primarily in a dry and wet region. The magnitude of heat flux and the gap size are found to be among the most important factors in crevice boiling phenomena.

In planar crevice experiment, the vertical temperature difference in the crevice increased as the heat flux increased. The measurement of pH using tungsten electrode was attempted but due to steam blanket pH signal in crevice could not be measured. It is found that heat flux controlled experiment causes overheated crevice and makes pH measurement difficult. The heating method using fluid or temperature controlled experiment is planned for the next step.

Acknowledgement

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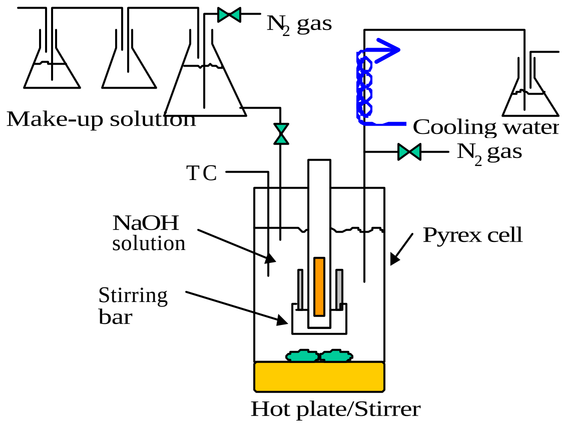

Figure 1. Schematic view of experimental apparatus for tubular crevice experiment.

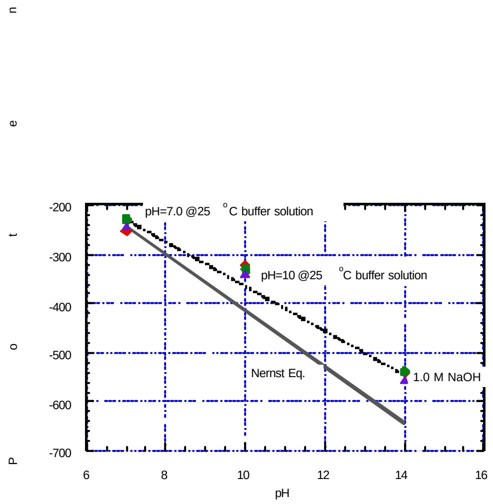

Figure 2. Potential of tungsten vs. Ag/AgCl (0.1 M KCl) reference electrode at 14 °C and atmospheric condition (tungsten: +, Ag/AgCl: -).

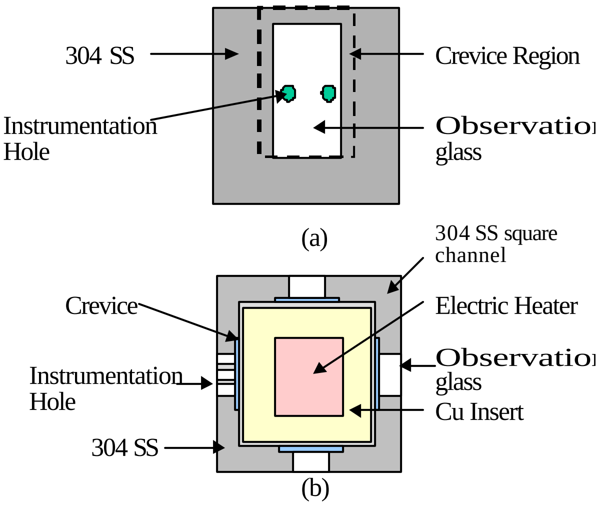

Figure 3. Schematic of (a) side view and (b) section view for planar crevice parts for planar crevice experiment.

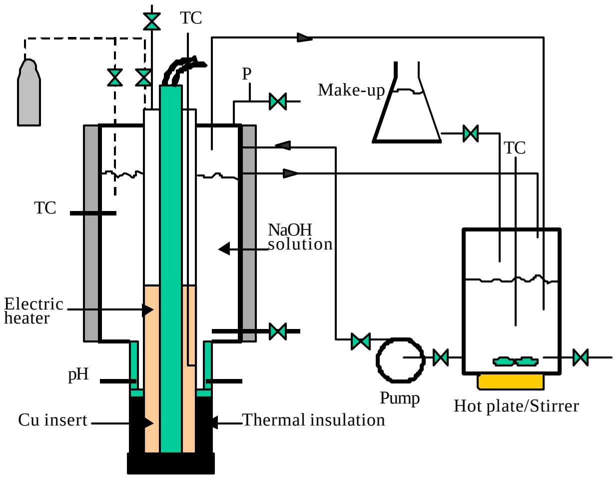

Figure 4. Schematic diagram of experimental apparatus for planar crevice simulation experiment.

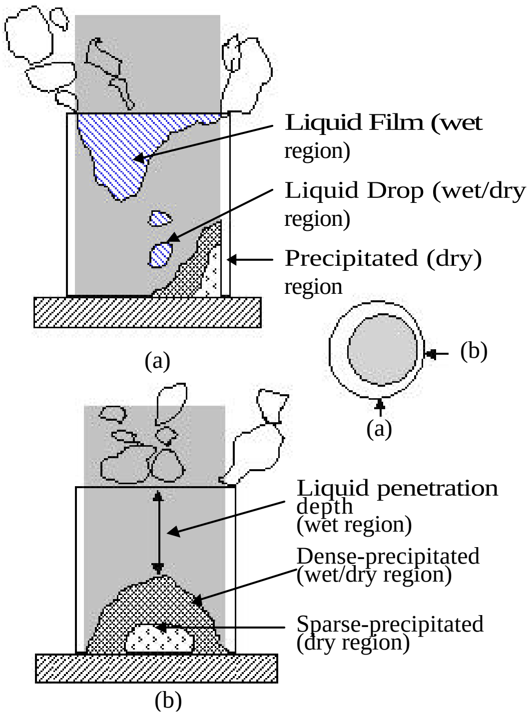

Figure 5. Sodium concentration features for (a) wider crevice gap region and (b) narrow crevice gap region with precipi- tation after 8-days experiment at such conditions as atmospheric, static, 200 ppm NaOH, and about 33 kW/m^2 heat flux.

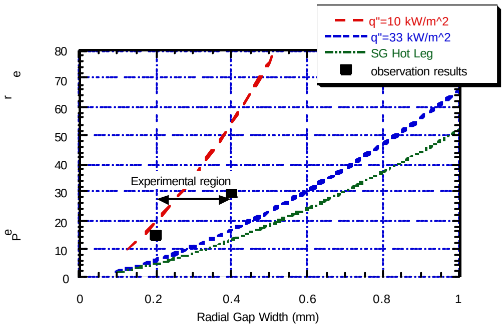

Figure 6. Composition with experimental results and analytical model for liquid penetration depth.

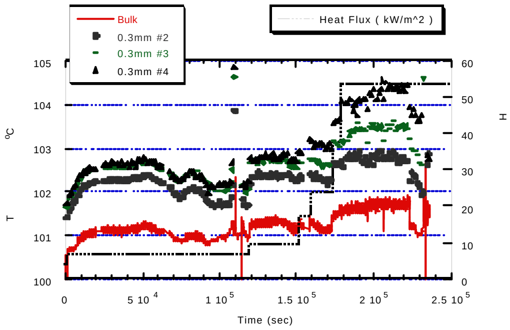

Figure 7. Temperature histories at the planar crevice of 0.3 mm gap and the variation of heat flux. (Thermocouples' location is as follows: #2-z/L=0.4, #3-z/L=0.6, #4-z/L=0.8.)

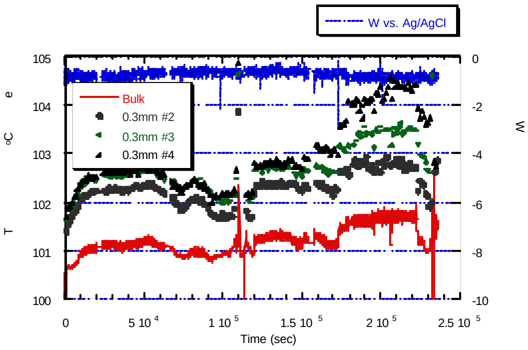

Figure 8. The potential of tungsten electrode vs. Ag/AgCl (0.1 M KCl) reference electrode.