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The effect of PAA on NaCl hideout in a simulated steam generator crevice

Dyiann Chou
San Jose State University

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**THE EFFECT OF PAA ON NaCl HIDEOUT IN A SIMULATED STEAM
GENERATOR CREVICE**

A Thesis

Presented to

The Faculty of the Department of Chemical Engineering

San Jose State University

In partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Dyiann Chou

August, 2000

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A handwritten signature in cursive script, appearing to read "Melanie McNeil", written over a horizontal line.

Dr. Melanie McNeil

A handwritten signature in cursive script, appearing to read "A. Diaz", written over a horizontal line.

Dr. Art Diaz

A handwritten signature in cursive script, appearing to read "Nikki A. Torigoe", written over a horizontal line.

Nikki A. Torigoe, EPRI

APPROVED FOR THE UNIVERSITY

A handwritten signature in cursive script, appearing to read "James H. [unclear]", written over a horizontal line.

ABSTRACT

THE EFFECT OF PAA ON NaCl HIDEOUT IN A SIMULATED STEAM GENERATOR CREVICE

By Dyiann Chou

A simulated steam generator and tube support crevice assembly was used to study the effect of porosity and addition of polyacrylic acid (PAA) on mass accumulation of impurities, temperature profile and superheat in the crevice. The system was operated at saturation conditions of 525 °F and 871 psig. Feed solutions of various combinations of NaCl, PAA, baked PAA and ETA at each crevice porosity were utilized to characterize the effect of addition of PAA. It was shown that the runs conducted with 30% packing porosity do not show any effect resulting from PAA. Results from the runs conducted with 20% packing porosity show that the total salt accumulation ratio of DI+NaCl+PAA+ETA runs to the DI+NaCl+ETA runs is about 0.24. The temperature profile of the DI+NaCl+PAA+ETA runs had an obvious concentration process at the center of the crevice after 3-5 hours operation. Steam blanketing effect can be confirmed from the crevice temperature profile of DI+NaCl+PAA+ETA runs. The ratio of total salt accumulation for 30% to 20% porosity is 0.88 for DI+NaCl+ETA runs.

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1.0 Introduction

1.1 History

Since 1957, when the first commercial nuclear fuel power plant in the United States was established, corrosion in steam generators has been a regular and serious problem (Cocks, 1973). Although most types of corrosion damage have been eliminated over the past three decades, the major technical problem that is threatening the nuclear power industry today is localized corrosion in pressurized water reactor steam generators (Douglas, 1995); specifically, corrosion that occurs in the crevices between the steam generator tubes and tube support plate.

1.2 Economic Impact

This kind of corrosion is a great ongoing expense for the nuclear power industry. Generally speaking, the first-generation steam generators for commercial nuclear power plants, built in the late 1950s, were designed to last for about forty years. However, most of them were beginning to deteriorate within eight to ten years of commissioning. This premature deterioration led to considerable expense for the

replacement of steam generators and the maintenance of existing steam generators.

The average cost of steam generator replacement is \$100-200 million, and the maintenance of existing steam generators can cost up to one million dollars per day due to extended outages and forced plant shutdowns (Douglas, 1995). Despite the progress made in correcting many kinds of corrosion problems, further research and experimentation is needed to find and implement cost-effective solutions to the remaining corrosion problem in tube and tube support plate crevices.

1.3 Functional Background

An understanding of the basic operation of a nuclear power plant, as shown in Figure 1.1, will help to explain this corrosion problem. Primary water circulates from the reactor core to the steam generators through 15,000 to 30,000 tubes at a pressure of 2250 psia, after which the primary water is recirculated back to the core. The heat from the primary water is transferred through the tubing in the steam generator to the secondary water, which is heated to boiling at 770-1050 psia. The steam thus generated drives the electrical power generating turbines. After leaving the turbines, the steam passes through a condenser; the condensed secondary water is then

Figure 1.1 Reactor core and nuclear steam supply system (NSSS) of a typical pressurized water reactor (Ref.: B. M. Ma, Nuclear Reactor Materials and Applications, 1983, p. 1.)

purified in resin beds, and returned to the steam generator (Parkings, 1982).

1.4 Corrosion Problems in Steam Generators

Steam generators undergo various forms of corrosion damage. Douglas listed six major types of corrosion problems and their location in the pressurized water reactor steam generator. They are U-bend primary-side stress corrosion cracking, antivibration bar wear, pitting, secondary-side intergranular attack, tube denting, and secondary-side stress corrosion cracking. The U-bend primary-side stress corrosion cracking and antivibration bar wear occur at the tube with U-shape and the tube held by antivibration bar. The pitting and secondary-side intergranular corrosion problem usually occurs between the tube sheet at the bottom of the steam generator. Tube denting and secondary side corrosion cracking are the corrosion problems which most commonly are seen in the tube and tube-support plate crevices. Some of the corrosion problems have been virtually eliminated, others are being successfully managed, and a few have not yet been brought under control. According to reports prepared by Douglas in 1995, a large number of older plants experience two major kinds of tube deterioration that are now threatening to limit the useful life

of many steam generators – secondary-side stress corrosion cracking and tube denting, as shown in Figure 1.2.

1.5 Mechanisms of Corrosion and Hideout

Crevice corrosion problems are attributed the local concentration effects of aggressive solutes and impurities in restricted region. In addition to the impurities and restricted region, heat flux across the crevice is an another important factor that is required to cause the crevice corrosion problems. From the studies of clean crevice conducted by Wang, Pan and Tsai in 1990 and Rogers in 1997, a clean crevice will not accumulate a relevant amount of sodium chloride because there is no flow restriction to bulk solution. For a non-uniform crevice, from the results of previous researchers, impurities accumulated since a flow restriction area is created in the crevice.

Studies on the mechanism of crevice impurity concentration in pressurized water reactor steam generators have been performed since 1980, with one of the most important study being the review paper written by Millett and Fenton in 1990. The corrosion in tube and tube support plate crevices occurs as a self-sustaining process. First, the carbon steel of both tube and support structure acts as an anode which

**Secondary-side stress
corrosion cracking**

Figure 1.2 Diagram illustrating tube denting and secondary-side stress corrosion cracking. (Ref.: J. Douglas, "Solution for Steam Generators", EPRI Journal May/June 1995.)

interacts with oxygen in the water, and bulky corrosion products, as described by Potter and Mann in 1965, are generated in the crevice between the tube and its supporting structure (Potter, 1997). According to the research done by Hermanson in 1993, iron in the form of magnetite (Fe_3O_4) is the predominate component of the corrosion product (Hermanson, 1993). After the corrosion process begins, the oxygen in the crevice water become insufficient due to restricted flow of bulk water into the crevice. The lack of oxygen causes the migration of chloride to the crevice, as shown in Figure 1.3, where the chloride is from the secondary water containing various impurities it picks up in the condenser (Parkins, 1982). In turn, the negatively-charged chloride draws positively-charged sodium from the bulk water into the crevice. Generation of steam on the outer surface of the heat exchanger tube causes sodium chloride to precipitate in the crevice. Because it is a narrow channel, the crevice is a region where the flow of water, and thus the transport of mass, are restricted. The restricted mass transport in the crevice further concentrates the sodium chloride impurities in the crevice. When corrosion product accumulates, the flow of water becomes even more restricted. Since a restricted amount of water flows through the crevice, the concentration of salts in the crevice keeps increasing. In

Figure 1.3 Mechanism of crevice corrosion. (Ref.: S. O. Kasap, Principle of Electrical Engineering Materials and Devices, McGraw-Hill, 1997, p. 740)

addition, because heat transfer is relatively low in the crevice, localized boiling and evaporation further increases the salt concentration there. This concentration of salt in the crevice is commonly referred to as “hideout.”

The corrosion products thus continue to accumulate in the form of porous deposits in the crevice between the heat exchanger tubes and the tube support structures, resulting in fouling of the crevice, even more restricted water flow, and an even more aggressively corrosive environment (Millet, 1990). This ongoing process of corrosion weakens the tube and support structure, increasing the stresses on both. The stresses thus caused are sufficient to mechanically deform the tubes and crack the tube supports.

1.6 Corrosion Control by Water Chemistry

To minimize corrosion, water chemistry is controlled in pressurized water reactor steam generators. Two major schemes are used to control the chemistry of secondary water in pressurized water reactors. First, in the early 1970s, recirculating steam generators were used for this purpose. Then, steam generator chemistry was controlled using sodium hydroxide and disodium phosphate to maintain pH. In

addition, hydrazine or sodium sulfates were used to control or scavenge oxygen in steam generators. This type of water control still resulted in thinning corrosion of the tube walls. Therefore, the All Volatile Secondary Water Treatment (AVT) was introduced (Millet, 1995). The All Volatile Secondary Water Treatment involves the treatment of the secondary water with the addition of hydrazine and ammonia. The hydrazine scavenges for dissolved oxygen, and the ammonia controls pH. This method solved the thinning or wastage corrosion problem, but resulted in tube denting. Millet then further introduced an approach to controlling the chemistry of the water in the crevice based on a target molar ratio indicator. The practice of Molar Ratio Control is based on the assumption that the crevice water pH can be modified by controlling the ratio of strong acid anions and strong basic cations in steam generator bulk water (Millet, 1995).

Douglas summarized the corrosion problems occurring in steam generators and the solutions for each type of corrosion problem in 1995. Most of the corrosion problems have been either eliminated or successfully managed except secondary-side stress corrosion cracking due to the local concentration effect in tube support crevices. Barkatt studied the effects of ethanolamine (ETA), pH change and increased

hydrazine levels on deposit-covered alloy 600 and brass corrosion. The tests showed that the introduction of ethanolamine and a moderate increase in pH brought about lower corrosion rates, but enhancement of hydrazine levels caused corrosion rates to rise. In the case of brass, tests with ETA and hydrazine showed that increasing the pH caused the corrosion rates to increase, but the introduction of ETA led to a mild decrease in these rates (Barkatt, 1997). More research is needed to study the effects of additions on corrosion.

1.7 Polyacrylic Acids

Polyacrylic acids have been added to steam generators to reduce the accumulation of impurities in the crevice. These are weak acids and act as dispersant chemicals to maintain the corrosion products in suspension long enough so that a significant amount can be removed from the system before deposition occurs. The chemical structure of polyacrylic acids is shown in Figure 1.4:

Figure 1.4 The chemical structure of polyacrylic acids

Since the mass concentration of the polyacrylic acids in the steam generator may be much larger than any non-water component present, Miller studied the chemistry of polyacrylic acids and its thermal decomposition products in the secondary cycle of a pressurized water reactor. The results showed that the main effect of polyacrylic acid chemistry appears to be a small lowering of the pH in the steam generator. In another words, it is favorable for a solution to reduce its pH with the addition of PAA. Much uncertainty still remains as to the effects of polyacrylic acids on the secondary water chemistry.

2.0 Literature Review

2.1 Hideout Studies

2.1.1 Mann and Castle (1983)

Although the mechanism of salt hideout has been studied in the past 20 years, experimental studies investigating the concentration effect in steam generator crevices were quite limited until the early 1980s. In 1983, Mann and Castle developed a model which can be applied to the tube – support plate crevice in pressurized water reactor steam generators. They constructed small-scale simulated crevices with both ends open as shown in Figure 2.1 and employed ion-specific electrodes to measure the concentration effect in the tube-support plate crevice. The model tests were operated in an autoclave housing a simulated tube and tube support plate. The electric heater/crevice heater, consisting of an Inconel tube, internal cartridge heater and a low-melting alloy between the tube and the heater, simulates the primary water side of a heat exchanger tube. The one-liter autoclave, which simulates the steam generator, was pressurized to 64 bar and heated to 280°C to simulate the secondary – side environment of a typical steam generator. Carbon fibers with 56% porosity were

Figure 2.1 Diagram of heated crevice (Ref.: G. M. W. Mann and R. Castle, "Salt Concentration in Heated Crevices and Simulated Scale," EPRI NP-3050, October, 1983)

packed into the crevice to simulate the natural deposition of porous material from corrosion products. In order to monitor the axial concentration distribution of the solution in the crevice, thermocouples were soldered along the heating surface of the electric tube heater, not in the crevice itself. Ion-specific electrodes measured Na and Cl concentrations at the autoclave outlet. Finally, the concentration profile was numerically integrated to give the total mass of the accumulated salt in the crevice (Mann and Castle, 1983).

The experiments of Mann and Castle resulted in some important findings. Figure 2.2 shows the weight of sodium chloride in crevice. Initially, the rate of salt accumulation is constant before an equilibrium weight of salt is reached. The rate of salt hideout increased with the bulk water concentration and was little affected by heat flux over the ranges studied. The total amount of salt accumulated increases as the heat flux increases and, to a smaller effect, increases with increasing bulk water NaCl concentration as shown in Table 2.1. The total accumulated salt was found to increase with increasing available superheat where available superheat as defined as the temperature difference between the heater tube wall and the bulk solution. The greater the available superheat, the more salt that accumulates in the crevice. Salt

Figure 2.2 Weight of sodium chloride in crevice (Ref.: G. M. W. Mann and R. Castle, "Salt Concentration in Heated Crevices and Simulated Scale," EPRI NP-3050, October, 1983)

Table 2.1 Initial rates of accumulation and equilibrium weights of salt in crevice. (Ref.: G. M. W. Mann and R. Castle, "Salt Concentration in Heated Crevices and Simulated Scale," EPRI NP-3050, October, 1983)

Heater power (Watts) and equivalent bare tube heat flux (kW/m ²)	85	150	150	150	230
Feed concentration (mg/kg NaCl)	12	120	12	1.2	12
Rate of salt accumulation (mg/hour)	-	14.4	2.28	0.144	3.86
Equilibrium weight (mg NaCl)	1.1	13	8.2	5.7	35
Mean concentration in crevice (g/l NaCl)	8.5	100	63	44	270
Mean concentration factor	700	800	5000	36000	22000
$\frac{\text{Equilibrium weight}}{\text{Rate of Accumulation}}$ (hours)	-	0.90	3.6	39	9.1
Calculated rate of salt accumulation (mg/hour) *	1.78	31.5	3.15	0.315	4.83
Concentrating efficiency (Observed/theoretical rate)	-	0.46	0.72	0.46	0.80

* $0.75 \times \text{heater power} \times \text{feed concentration} \div \text{latent heat of evaporation}$

accumulated rapidly above a critical level of available superheat; in turn, as the amount of salt in the crevice increased, the available superheat that is required to cause salt accumulation appeared to decrease. Salt initially concentrate at the center of the crevice, and this result leads to the elevation of the boiling point of the solution in the central part of the crevice. As salt continues to accumulate, the temperature rise spreads to the upper and then lower end of the crevice. Finally, they observed that the salt was rapidly released from the crevice into the bulk water when the heater was switched off during the return phase, as shown in Figure 2.3. Based on these results, they developed a non-uniform concentration model to describe the behavior of salt hideout as shown in Figure 2.4.

2.1.2 Wang, Pan and Tsai (1990)

In 1990, Wang, Pan, and Tsai used an autoclave, water treatment, and a monitoring system to simulate the secondary side of a steam generator and investigated the hideout phenomena of sodium chloride in a tube support-plate-crevice. The crevice used in this study was open on both ends of the crevice. However, they ran the experiment at atmospheric pressure. The hideout phenomena

Figure 2.3 Typical surge in outlet concentration after switching off the crevice heater (Ref.: G. M. W. Mann and R. Castle, "Salt Concentration in Heated Crevices and Simulated Scale," EPRI NP-3050, October, 1983)

Figure 2.4 Model of solute concentration in heated crevice. (Ref.: G. M. W. Mann and R. Castle, "Salt Concentration in Heated Crevices and Simulated Scale," EPRI NP-3050, October, 1983)

they investigated included the effect of heat flux, bulk concentration, crevice width, and the presence of a porous medium. These parametric studies advanced the understanding of the concentration effect in the support-plate crevice.

The experimental setup is similar to that used by Mann and Castle. The amount of solute hideout in the crevice was measured by monitoring the conductivity in the designed loop using a conductivity cell. Thermocouples used to measure the crevice temperature were soldered along the wall of heating crevice. The crevice was packed with carbon fiber, in the form of a 7 micron diameter braided tube, resulting in a calculated porosity of 74%. The major difference from Mann and Castle is that the studies were performed under 1 atm of pressure. The results they observed from their experiment are as follows:

- 1. The solute concentrates heavily near the upper end of crevice as determined by the higher temperature measured by thermocouple located at the upper end of the crevice. This result is consistent with Mann and Castle's findings.**
- 2. An axial concentration distribution of corrosion product is confirmed as determined by the different temperature measured from all the thermocouples along the crevice wall. This result is consistent with Mann and Castle's findings.**

3. The hideout rate increases with increasing heat flux and bulk NaCl concentration.

The effects of the heat flux and bulk concentration were relating close to equal.

This result differs somewhat from Mann and Castle's observation that “the rate of salt hideout increased with the bulk water concentration and was little affected by heat flux over the ranges studied.”

4. The total mass accumulation increases with increasing heat flux and bulk concentration and with decreasing crevice width. Although heat flux plays a more important role on the effect than bulk NaCl solution and crevice width there is some deviation compared with Mann and Castle's results. The total amount of salt accumulated is increased with the heat flux, but the increase with bulk water solution is much less, as shown in Table 2.1.

5. The presence of a porous medium in the crevice significantly enhances the concentration effect.

In the studies performed by Wang, Pan, and Tsai, they measured the amount of salt hideout in the crevice was measured by monitoring the total conductivity in the closed loop using a conductivity cell.

2.1.3 Balakrishnan (1991)

In 1991, Balakrishnan studied the hideout of salt mixture of sodium chloride, sodium sulfate and calcium chloride in both carbon fiber and carbon powder packed crevice at a constant superheat and varied heat flux. They found that hideout proceeded at a linear rate until the crevice was saturated. The hideout rate was entirely determined by the heat flux in the crevice. No preferential hideout of one species over another was observed. Balakrishnan studied the temperature distribution in both carbon fiber and carbon powder packed crevice, as shown in Figure 2.5 and Figure 2.6. Obviously, the temperature in the carbon fiber packed crevice tended to increase after turning on the crevice heater tube with constant power supply (Balakrishnan, 1991). It is normal that all temperatures in the crevice increase with time. However, from Figure 2.6, the temperature at the center of the crevice decreased because of steam blanketing, which will be discuss in detail later. They also monitored how the effluent pH change during a typical test as shown in Figure 2.7. The pH went as high as 10.5 during the return phase, while the feed solution pH was about 6. Similar results were obtained for some other tests. As shown in Table 2.2, the pH went as high as 11.3 in one test, over 10.3 in three tests and

Figure 2.5 Temperature distribution in the carbon fiber packed crevice. (Ref.: P. V. Balakrishnan, "Hideout and Return of Complex Mixtures in Crevices," EPRI NP-7494, September, 1991)

Figure 2.6 Temperature distribution in the carbon fiber packed crevice. (Ref.: P. V. Balakrishnan, "Hideout and Return of Complex Mixtures in Crevices," EPRI NP-7494, September, 1991)

Figure 2.7 Change in pH During Hideout and Return in Carbon Fiber Packed Crevice. (Ref.: P. V. Balakrishnan, "Hideout and Return of Complex Mixtures in Crevices," EPRI/NP-7494, September, 1991)

Table 2.2 Hideout return rate and maximum pH of effluent during return. (Ref.: P.

V. Balakrishnan, "Hideout and Return of Complex Mixtures in Crevices," EPRI

NP-7494, September, 1991)

Test	Hideout Time (h)	Release Rate $\times 10^4$ (s ⁻¹)			Ca	Max. pH
		Na	Cl	SO ₄		
Fibre-Packed Crevice:						
38	1.50	3.83	4.03	3.58	—	7.50
39	16.92	0.31	0.36	0.25	—	10.72
40	21.71	0.18	0.19	0.17	—	10.59
Powder-Packed Crevice:						
28	1.94	4.75	5.92	5.97	—	5.76
29	2.50	3.44	4.11	4.17	—	
32	1.13	2.25	3.11	3.61	—	
34	1.51	1.94	3.06		—	
35	1.96	5.08	5.14	4.94	—	6.80
41	19.39	0.51	0.58	0.43	—	8.09
42	21.05	0.72	0.83	0.62	—	11.29
45	21.25	0.32	0.39	0.21	—	10.31
47	43.00	0.51	0.65	0.32	—	8.29
48	67.50	0.52	0.53	0.58	—	8.96
49	19.25	0.48	0.37			8.00
50	89.83	0.26	0.34	0.05	0.33	9.89
53	44.00	0.77	0.71	0.03	0.11	6.76
54	64.50	0.40	0.59	0.33	0.16	6.40
55	88.25	0.38	0.34	0.36	0.57	9.87

over 8.0 in six tests. Preferential release of some cationic species with respect an anionic species would cause this effect.

Many researchers recognized that steam blanketing causes decreased hideout efficiencies. Steam blanketing occurs when steam bubbles fill the crevice. Steam bubbles take the place of concentrated solution in the crevice and lead to less hideout effect. In 1991, Balakrishnan found that steam blanketing had a direct effect on his studies. Steam blanketing can be investigated by observing the temperature profile in the crevice. He used three thermocouples, located separately at the top, middle, and bottom of the crevice, to measure the crevice temperature. Normally, all temperatures in the crevice should increase with time regardless of their location, as shown in Figure 2.6, which is the result of a carbon fiber packed crevice. However, as seen in Figure 2.5, the temperature profile plotted from the measurements of the thermocouples does not follow the normal behavior. The temperature at the center of the crevice decreased instead of increased due to reduced heat transfer coefficient.

2.1.4 Millet and Fenton (1994)

In 1994, Millet and Fenton performed several parametric studies to identify

important design and operating parameters. They found that the accumulation kinetics are a function of various parameters such as concentration of salt in the bulk water, crevice length, available superheat, diffusion coefficient, vapor/liquid distribution coefficient, and porous media permeability (Millet and Fenton, 1994). Several studies were done by previous scientists except the studies regarding available superheat, diffusion coefficient, and vapor/liquid distribution coefficient. As shown in Figure 2.8, Figure 2.9, and Figure 2.10, higher available superheat, higher diffusion coefficient, and higher vapor/liquid distribution coefficient results in higher concentration effect.

Then, Millet and Fenton developed a simple model of a dented and fouled tube support crevice to describe the transport processes in crevices (Millet and Fenton, 1990). In 1994, they developed a more detailed model of the processes of localized concentration of porous deposits in steam generators that describes the heat, mass, and momentum transfer process (Millet and Fenton, 1994).

2.1.5 Rogers (1997) and Coonradt (1999)

Paul Rogers characterized an experimental crevice by studying sodium chloride

Figure 2.8 Steady state concentration profile as a function of the available superheat. (Ref.: P. J. Millett and J. M. Fenton, "A Modeling Study of Parameters Controlling Local Concentration Processes in Pressurized Water Reactor Steam Generators," Nuclear Technology, Vol. 108, Nov. 1994, p. 256)

Figure 2.9 Steady state concentration profile as a function of the diffusion coefficient. (Ref.: P. J. Millett and J. M. Fenton, "A Modeling Study of Parameters Controlling Local Concentration Processes in Pressurized Water Reactor Steam Generators," Nuclear Technology, Vol. 108, Nov. 1994, p. 256)

Figure 2.10 Steady state concentration profile as a function of the vapor/liquid distribution coefficient. (Ref.: P. J. Millett and J. M. Fenton, "A Modeling Study of Parameters Controlling Local Concentration Processes in Pressurized Water Reactor Steam Generators," Nuclear Technology, Vol. 108, Nov. 1994, p. 256)

hideout in the simulated steam generator at San Jose State University in 1997. Feed solutions of 30, 60, 120 ppm sodium chloride and a crevice power of 85, 150 and 230 watts were used to characterize the experimental crevice. The porosity of carbon fiber packed in the crevice was 58% to simulate the corrosion products. Rogers concluded from his experiments that as the heat flux across the crevice was increased, the available superheat was increased resulting in a higher crevice concentration. He also found that the rate of accumulation was related to bulk water concentration and heat flux across the crevice. He also reported that the NaCl accumulation rate and equilibrium crevice concentration were 0.42 mg/min and 86 mg for a feed concentration of 120 ppm and a crevice heater power of 230 watts.

Scott Coonradt used exactly the same system as Rogers used. Basic form of PAA studies on NaCl accumulation were performed with the feed solution contains 50 ppm sodium chloride and 8 ppm basic form of PAA. The crevice was packed with carbon fiber resulted in 30% porosity. The feed solution was introduced to the system at 20 ml/min and The crevice heat power is held at 150 watts by power controller. The temperature in side the heater core was about 700 °F while the temperature at crevice wall was at 525 °F. Heater tube was turned on after the system reaches steady state.

Coonradt regarding the effect of basic form of PAA on sodium chloride hideout in simulated steam generator crevice reported no significant results.

Although there was no significant findings regarding the effect of basic PAA form on hideout return, he gained valuable experience while working on the study. First of all, he experienced preferential hideout while performing DI water runs to verify the contamination in the system. He found that the opposite reaction of hideout and return was observed with DI water runs. Right after the crevice heater was turned on, there was a large spike in specific conductance instead of a drop (Coonradt, 1999). He explained that this large spike indicates the preferential hideout of Na^+ was occurring. After the heater was turned on, Na^+ was hiding out while Cl^- continued flowing down the stream. Cl^- in the exit steam turned into HCl and left a large amount of H^+ and OH^- ions in the exit stream. Since the specific conductance of H^+ ($398 \text{ S-cm}^2/\text{mol}$) and OH^- ($198 \text{ S-cm}^2/\text{mol}$) is so much larger than Na^+ ($50.1 \text{ S-cm}^2/\text{mol}$) or Cl^- ($76.3 \text{ S-cm}^2/\text{mol}$), a large spike was observed in the exit stream (Coonradt, 1999).

Besides the contribution regarding the preferential hideout, he also approved a good repeatability of the system he was using by back-to-back run of DI+NaCl+ETA.

Back-to-back run of DI+NaCl+ETA was performed by running exactly the same batch solution with heater turned on and off twice, and without introducing DI run in between the two DI+NaCl+ETA runs. The error obtained from this experiment is less than 15%, which is good since many researcher experienced the error greater than 15% while doing hideout studies (Coonradt, 1999).

2.2 Crevice Packing

The packing materials used in steam generator crevices should have some special characteristics, such as tolerance of high temperatures. The packing materials could be carbon fiber, carbon powder, or oxide deposits. Different types of crevice packing materials and different morphology of the materials simulate different crevice corrosion products in steam generator.

Mann and Castle and Wang *et al.* used carbon fiber as a crevice packing material. Actually, carbon fiber has a different morphology from the actual corrosion products in the steam generator crevice (Mann and Castle, 1983).

Continuous channels will be created in the crevice parallel to the axis of the heat exchanger tube if carbon fiber is packed in the crevice. How the continuous channels

affect the solute concentration in the crevice is uncertain. However, it is believed that the solute might escape from the channels, leading to lower rates of accumulation.

In 1991, Balakrishnan studied the hideout of salt mixture in both carbon fiber and carbon powder-packed crevice. He found that the temperature in the carbon fiber packed crevice tended to decrease after turning on the crevice heater tube with constant power supply. However, the temperature in the carbon powder packed crevice tended to rise. From the differential temperature distribution in the crevice he concluded that, for the crevice packed with carbon fiber, the salt accumulated deep in the crevice initially and slowly spread out into the rest of the crevice. However, for the crevice packed with carbon powder, the salt accumulated initially at the mouths of the crevice and penetrated later on into the central region (Balakrishnan, 1991).

Different morphologies of the same packing material also resulted in different hideout efficiencies and created different superheats. Compared with the crevice packed with carbon fiber, the crevice packed with carbon powder had lower hideout efficiency and higher superheat than that packed with carbon fiber for the same heat flux.

2.3 Methods to Measure Salt Hideout

In the studies conducted by Mann and Castle in 1983, ion-specific electrodes were used to measure the sodium and chloride concentrations at the autoclave outlet.

Figure 2.11 shows the schematic presentation of a membrane electrode assembly.

Appendix N has further discussion on the electrode.

Balakrishnan successfully developed a on-line analysis system to monitor some specific ions using the ion-specific electrodes. Figure 2.12 shows the flow diagram of the on-line analysis system. The system consisted of three Lucite cells holding ion-specific electrode for Na, Ca, and Cl. Each of these electrodes was coupled to a reference electrode through a salt bridge, as shown in Figure 2.13. In the on-line analysis system, the solutions required for adjusting the ionic strength of the sample were mixed with a stream in a column away from the cell, as shown in Figure 2.12.

The program calibrated the electrodes using the two standard solutions at the beginning of the experiments, and then started on the measurements on the autoclave effluent. Readings were taken once every minute or two minutes from each electrode.

Besides, the samples from effluent were collected every certain time and were analyzed by ion chromatography or inductively coupled plasma-atomic emission

Figure 2.11 Schematic diagram of an ion-selective electrode. (Source: W. E. Mort and W. Simon, *Ion-Selective Electrode an Analytical Chemistry*, 1971, p. 267)

Figure 2.12 Flow diagram of the on-line analysis system. (Ref.: P. V. Balakrishnan, "Hideout and Return of Complex Mixtures in Crevices," EPRI NP-7494, September, 1991)

Figure 2.13 The electrode cell. (Ref.: P. V. Balakrishnan, "Hideout and Return of Complex Mixtures in Crevices," EPRI NP-7494, September, 1991)

spectrometry. Finally, the data from on-line analysis and off-line analysis was plotted on the same graph to make sure that the on-line analysis is accurate enough. Figure 2.14 shows the on-line and off-line results of the experiments conducted by Balakrishnan. Obviously, the results from on-line and off-line system are consistent.

Brunet and Campan used ^{24}Na as a radioactive tracer to study the concentration effects in both the support-plate and the tube-sheet plate (Brunet and Campan, 1987). They studied the mechanism for the sodium hideout and established analytical models based on the data generated from hideout, return and flushing experiments. In their experiments, the amount of Na accumulated in the crevice was computed from the measured radioactivity.

2.4 Decomposition of Polyacrylic Acids

Polyacrylic acids will decompose via decarboxylation and C-C bond scission in pressurized under water reactor steam generator operating conditions (Balakrishnan *et al.* 1990). The main decomposition mechanism is decarboxylation. Decarboxylation of polyacrylic acids will produce carbon dioxide and hydrogen. This is followed by stepwise progression to form a pure alkane or alkene hydrocarbon. In

Figure 2.14 Hideout return of sodium chloride in carbon fiber packed crevice. (Ref.: P. V. Balakrishnan, "Hideout and Return of Complex Mixtures in Crevices," EPRI NP-7494, September, 1991)

terms of the C-C bond scission, the low molecular weight acids will be formed.

The modeling study of the chemistry of polyacrylic acids in the secondary cycle of a pressurized water reactor was been performed by Miller in 1999. His research has two parts: modeling the polyacrylic acids, and modeling the polyacrylic acid decomposition products. In the first part of the study, he assessed the effect of polyacrylic acids on the chemistry of the secondary system and estimated the physical and chemical properties of the polyacrylic acids. Two sample solutions were tested. Sample 1 is composed of ETA (2ppm), NH₃ (50ppb), and hydrazine (120ppb). Sample 2 is composed of ETA (2ppm), NH₃ (50ppb), hydrazine (120ppb), and polyacrylic acids (10ppm). The result showed that sample 1 has a pH of 6.31 at 513°F (0.7 units above neutral) and sample 2 has a pH of 6.25 at 513°F (0.64 units above neutral). As a result, no significant change due to the addition of polyacrylic acids can be seen in secondary water.

The second part of the study was to model the polyacrylic acid decomposition products. Various decomposition mechanisms and decomposition products were noted. Miller predicted the distribution of the products from the degradation of polyacrylic acids. Carbon dioxide is the main decomposition product.

Miller reported that, with the decomposition rate constant of 0.14 hr^{-1} , polyacrylic acids are lost at a rate of 0.7lb per hour and CO_2 is generated at a rate of 0.4lb per hour. The second group of decomposition products is low molecular weight organic acids. They are the most noticeable decomposition products from polyacrylic acids. Among these three major low molecular weight acids, acetic acid will predominate based on its high thermal stability and stable physical properties. The other two low molecular weight organic acids from this decomposition include formate and glycolate. The low concentration of organic acid will not significantly impact the system pH or the cation conductance. The last group of decomposition products is aliphatic compounds. These pure organic products have no functional groups so that it is difficult for the reacting system to remove these non-ionic, non-volatile species (Miller, 1999).

Polyacrylic acids can be considered act as a surfactant. The nature of the surfactant is to reduce the surface tension and the capillary pressure. Since capillary pressure inhibits mixing of the liquid and vapor phases in the crevice, elevated capillary pressure enhances hideout effect in the crevice (Millet and Fenton, 1990). Consequently, addition of PAA is considered as a way to reduce surface tension, thus,

reduce the capillary pressure in the crevice, and finally, reduce the hideout effect in the crevice.

3.0 Hypothesis And Research Objectives

3.1 Hypothesis

The addition of polyacrylic acids in the feed water will decrease the maximum mass accumulation rate and the equilibrium mass accumulation of sodium chloride in the packed crevice of the simulated steam generator. On the other hand, polyacrylic acids decompose during baking (Miller, 1999), breaking down into short fragments and losing polymer properties. Therefore, baked polyacrylic acids will have less effect on reducing the maximum mass accumulation rate and the equilibrium mass accumulation of sodium chloride than unbaked polyacrylic acids.

3.2 Objectives

The objectives of this research are to study the effect on sodium chloride hideout in a simulated steam generator crevice of: (1) the addition of polyacrylic acids, and (2) different carbon fiber packing at two levels of porosity. The major relationships that will be studied in a crevice packed with carbon fiber of 30% and 20% porosity are:

- 1. The effect of polyacrylic acids and baked polyacrylic acids on the mass accumulation rate of sodium chloride within the packed crevice.**
- 2. The effect of polyacrylic acids and baked polyacrylic acids on the total equilibrium mass accumulation of sodium chloride within the packed crevice.**
- 3. The effect of polyacrylic acids and baked polyacrylic acids on superheat.**

- 4. A comparison of the results for carbon fiber of 30% porosity with carbon fiber of 20% porosity.**

3.3 Justification

The major engineering goal for the nuclear power industry is to minimize the corrosion problems in pressurized water reactor steam generators. These corrosion problems have created a great ongoing expense for the nuclear power industry. In the past ten years, the Electrical Power Research Institute has made several important advances in managing corrosion problems. Some guidelines to prevent the corrosion problems in steam generators were developed, for example, the guideline to control the steam generator feed water chemistry. Several chemicals, such as ETA, hydrazine, amines, and polymers are added to steam generator feed water to change the chemical properties of the feed water in order to prevent most of the corrosion processes. Unfortunately, some complicated corrosion problems, such as intergranular stress corrosion cracking, still exist. In the current study, a lab-sized simulated steam generator will be utilized in experiments to understand how polyacrylic acids affect the mechanism for concentrating impurities in steam generator. Hopefully, by doing this research, a better solution can be found to achieve the goal of minimizing corrosion problems.

4.0 Materials And Methods

The apparatus that was used in this study consists of an autoclave enclosing an experimental simulated steam generator crevice, a feed system at the entrance, a monitoring system at the exit, an automatic data acquisition system, and a water purification system. The components of each system will be addressed in detail later. The schematic diagram of the flow loop is illustrated in Figure 4.1.

4.1 Apparatus

4.1.1 Simulated Steam Generator and Crevice

A 1-liter autoclave fabricated by Rockwell International from Inconel alloy 718, as shown in Figure 4.2, simulates the pressurized water reactor steam generator. The test solution enters the autoclave through an inlet located approximately 1 inch from the bottom and exits approximately 0.5 inch from the top, as shown in Figure 4.2. The test solution in the autoclave simulates the water in the secondary side of the steam generator. Fuji Electric temperature controllers control the temperature of the bulk solution in the autoclave with power provided by three Omega resistance band heaters.

Rockwell International also has constructed the experimental tube and tube-support crevice cage assembly used in this study. Figure 4.2 shows the schematic of the crevice cage assembly. The alloy 600 electric heater tube as shown in Figure 4.2 simulates the primary water side of the heat exchanger. Inside the tube is a 600 watt

Figure 4.1 The schematic diagram of the flow loop.

Figure 4.2 Schematic diagram of autoclave and crevice.

cartridge heater surrounded by a eutectic salt mixture consisting of 54.3 wt % KNO_3 and 45.7 wt % NaNO_3 . The eutectic salt melted at about 250°C and is included in order to enhance the heat transfer to the tube wall. The cartridge heater is longer than the crevice and it is assumed that the generated heat is uniformly distributed. Eight K-type thermocouples are soldered along the inner surface of the heater tube, equally spaced in a helical arrangement, as shown in Figure 4.3, to measure the temperature of the heater tube wall. Two separate K-type thermocouples are located inside the cartridge heater to measure the temperature of heater cartridge. Another thermocouple measures the temperature of the eutectic salt.

The actual crevice, which is open at both ends, consists of two half-sections of the clam-shell crevice ring, as shown in Figure 4.4, and is held by two support rings. Each supporting ring also has two ring assemblies containing two Teflon rings, which swelled under normal operating conditions to form an effective seal to keep fluid from entering the supporting ring and to straighten out the cage device attached to the crevice heater tube. Therefore, a simulated tube support crevice is formed which was concentric to the crevice heater tube. The length of the crevice is 30.5 mm and the gap that is formed between the alloy 600 tube and the alloy 718 center clam-shell ring is 0.24 mm in diameter. This gives a total crevice volume of 447mm^3 .

4.1.2 Entrance Supporting System

The entire feed system, shown in Figure 4.1, utilized 316 stainless tubing with

Figure 4.3 Schematic diagram of heater tube and thermocouples.

Side View

Figure 4.4 Schematic detailing half of the clam-shell crevice ring.

a 0.035-inch wall thickness. Nitrogen gas was bubbled through the test solution which was contained in a 60-gallon Nalgene feed tank to deoxygenate it. The Pulsar hydraulic diagram metering pump was set to pump the test solution through the system at a constant flow rate of 20 ml/min. Since the pump produced a large pulse, a pulse dampener was needed. The pulse dampener consisted of 25 feet of 1/16-inch PEEK (poly/ether/ether/ketone) tube. Downstream from the pulse dampener are a check valve, a pressure gauge, and a plug valve as shown in Figure 4.1. The purpose of the check valve is to prevent the test solution from flowing in the reverse direction in the system. It is important to keep the solution flowing in the forward direction so as not to cause pump failure. Two plug valves were installed at both sides of the autoclave to isolate the autoclave if necessary. The oven from a gas chromatograph 5790 Hewlett Packard with an oven temperature limit of 425°C was used as a pre-heater to heat the solution before it entered the autoclave.

4.1.3 Exit Supporting System and Monitoring System

A condenser was connected downstream from the autoclave to cool the test solution to room temperature. Then, the test solution flowed through a pressure relief valve and back pressure regulator and entered the monitoring system. The pressure relief valve was designed to release the pressure in an emergency situation so that the pressure never exceeded 1200 psia. The back pressure regulator with a maximum operating range of 1000 psia was installed to maintain the system

pressure at the desired pressure of 870 psig. The test solution flowed through the monitoring system before emptying into a waste tank.

The monitoring system monitored the flow rate, conductivity, and pH of the test solution from the autoclave as shown in Figure 4.1. It consists of a Standard Low Flow Rotometer, Alicat Volumetric Liquid Flowmeter, a Cole-Parmer sodium-specific electrode, a Cole-Parmer chloride-specific electrode, a Cole-Parmer pH probe, a Cole-Parmer total conductivity cell and a temperature probe. The Alicat Volumetric Liquid Flowmeter is connected to a data acquisition system to measure the flow rate downstream from the Standard Low Flow Rotometer. To measure the concentration change of sodium and chloride ion during the experiment, a Cole-Parmer sodium-specific and a Cole-Parmer chloride-specific electrode were installed. Thus, preferential hideout of one ion over another could be investigated by using these ion-specific electrodes. One Cole-Parmer pH probe and a pH meter were hooked to the system to monitor the pH change during the experiment. In addition, one Cole-Parmer conductivity flow cell with one Cole-Parmer conductivity meter with an accuracy of ± 0.3 was installed to measure the total conductivity at the autoclave exit. All the measurements obtained from the monitoring system were recorded once per minute by a PC-based data acquisition system.

The PC-based data acquisition system has several elements including a personal computer, transducers, signal conditioning hardware, data acquisition hardware, analysis hardware, and software. Figure 4.5 shows the elements of the

Figure 4.5 Elements of a PC-based data acquisition.

PC-based data acquisition system. The software used is LabVIEW from National Instruments.

4.2 Experimental Preparation

4.2.1 Water Preparation

De-ionized (DI) water obtained from a Barnstead water purification system was used to make up all feed solutions. This system consisted of a reverse osmosis system, a NANOpure deionization system, a storage system, and a water conditioner control system. Nitrogen gas, which was supplied by a high-pressure gas tank, was bubbled through the de-ionized water to deoxygenate it before it was used in the experiment. Some simple water tests, including conductivity measurement, pH measurement, and temperature measurement were taken to ensure the quality of the de-ionized water before it was used in the preparation of the feed solutions.

4.2.2 Chemicals Used

Table 4.1 lists the chemicals used to prepare the test solutions. The sodium chloride used in the experiment was optical-grade crystals of 99.99% purity. A solution of 8.7w% polyacrylic acid, which had an average molecular weight of 150K, was obtained from the Electric Power Research Institute. The baked polyacrylic acids were obtained by baking the polyacrylic acids for 6 hours at a temperature of 280°C and a pressure of 870 psig in the autoclave. Ethanolamine (ETA), which is a

strong base and is commonly added to the secondary water of steam generators to prevent corrosion, was also obtained from the Electric Power Research Institute. It was a solution in a concentration of 99.7% and was used to adjust the pH of the test solution.

Table 4.1 List of chemicals used to prepare the test solutions.

Chemicals	Formula	Description
Sodium Chloride	NaCl	Neutral Optical grade crystals of 99.99% purity
Polyacrylic Acid	$-\text{CH}_2-\text{C}_2\text{H}_2\text{O}_2-$	Weak acid Average molecular weight of 150K in a solution of 8.7wt%
Ethanolamine	$\text{HOCH}_2\text{CH}_2\text{NH}_2$	Strong base Concentration of 99.7%

4.2.3 Feed Solution Preparation

Three different feed solutions were used in this experiment. It was necessary to check the pH value and the conductivity of the DI water before making the feed solution to make sure that the DI water had a pH of around 5-6 and a conductivity near zero. Once the quality of the DI water was verified, a DP200 programmable pump was calibrated and 50.00L D.I. water was measured into the tank.

In runs which included NaCl, a 25 ppm NaCl solution was prepared. The desired amount of NaCl was added to the DI water, and mixed well with a Cole-

Parmer mixer. The corresponding conductance of the solution was checked to make sure it corresponded to a 25 ppm NaCl solution. The amount of PAA needed was weighed out with an electronic balance and added to the feed tank when required. ETA was added with a micropipette to adjust the solution to the desired pH value of 9.7-9.8. Several different feed solutions were prepared. They were 25 ppm sodium chloride solution with ETA (DI + NaCl + ETA), 25 ppm sodium chloride solution with ETA and 10 ppm PAA (DI + NaCl + PAA +ETA), 25 ppm sodium chloride solution with ETA and 10 ppm baked PAA (DI + NaCl + bPAA + ETA). A checklist for the preparation of the first two feed solutions is shown in Appendix A which illustrates the detailed procedure of making a feed solution.

4.2.4 Crevice Packing

Since a clean crevice does not accumulate salt, packing material was required to initiate the salt accumulation process in the crevice. The packing material restricts the flow of the solution through the crevice. The packing material used in this experiment is Thornel P-75S carbon fiber, which simulates the porous corrosion products in the crevice.

Carbon fiber of two different void fraction porosity levels were tested. One was 30% porosity, and the other was 20% porosity. Since the total volume of the crevice was known, the exact volume of carbon fiber needed to pack the crevice was calculated from the following equation:

$$\text{Porosity (\%)} = (V_{total} - V_{void}) / V_{void} \quad [1]$$

where V_{total} is the total crevice volume which is 0.447 cm^3 , V_{void} is the volume of carbon fiber packed in the crevice, and the porosity is the desired packing porosity of the fiber in the crevice.

Once the volume of carbon fiber needed to be packed in the crevice was obtained, the weight of carbon fiber needed can be calculated by multiplying the V_{void} by the density of the carbon fiber:

$$\text{Weight (carbon fiber)} = V_{void} \times \text{Density (carbon fiber)} \quad [2]$$

where the density of the carbon fiber is 2.0 g/cm^3 , which is known from the manufacturer's specifications.

The carbon fiber was cut into strands 3-cm in length and weighed out to the exact amount needed. The carbon fibers were laid in a crosshatch pattern to form 2 square mats, each 3 cm on a side and of identical weight. One mat was placed on each side of the clamshell crevice which was then connected together.

4.3 Experimental Matrix

4.3.1 Background Variables and Variables Measured

According to the parametric studies done by Wong in 1991 and Millet in 1995, several factors may affect the sodium chloride hideout return behavior. It is therefore important to understand which variables are background variables that need to be fixed throughout the experiment. The operating conditions of the secondary water in a real steam generator typically results in a bulk water temperature of 525°F and a system pressure of 870 psig. The experimental

conditions must simulate these observed real-world conditions. So the background system pressure and temperature of the bulk solution were set at 870 psig and 525 °F. Before the test solution entered the autoclave, it was heated in the oven which was set to 525°F (273°C). Different crevice heater powers (resulting in different temperatures) and different crevice lengths lead to different levels of salt accumulation in the crevice. In this study, these two variables were fixed also by porosity. The literature review revealed that packing in the crevice is needed to initiate salt accumulation in the crevice; a clean crevice does not accumulate salt. In this study, two sets of experiments were conducted to study the effects of different levels of porosity of carbon fiber packing in the crevice. In each set of experiments, the packing porosity was held constant.

The background variables that were constant during the experiment were shown in Table 4.2. The variables to be measured are listed in Table 4.3.

4.3.2 Experimental Tests

Since various additions can contribute to the total conductivity, various combinations of these additions in the feed were run to determine baseline conditions. These runs were the DI+ETA, DI+PAA, DI+PAA+ETA, DI+baked PAA+ETA, DI+50% PAA+50%baked PAA+ETA. Since the main objects was to measure the effect of PAA and baked PAA on NaCl accumulation, most runs concentrated on these feed solutions which were compared to the control runs of DI+ETA+NaCl. ETA was added to each run to adjust the pH to a confirmed initial value of 9.7-9.8.

Table 4.2 List of background variables that were fixed

Background Variables	Set Point
Pressure of the system	Held constant at 870 psig
Temperature of bulk solution	Held constant at 525°F
Temperature of pre-heater	Held constant at 273°C
Crevice heater power	Held constant at 150 watts
Crevice length	Held constant at 3 cm
Crevice volume	0.447 cm³
Porosity	30% for group 1 and 20% for group 2

Table 4.3 List of variables measured

Variables to Be Measured
1. Temperature of heater wall ($T_{\text{heater wall}}$)
2. Temperature of bulk solution (T_{bulk})
3. Total conductivity at exit (σ_{total})
4. Sodium concentration at exit (σ_{sodium})
5. Chloride concentration at exit (σ_{chloride})
6. pH value at exit (pH_{exit})

The purpose of using the baked form of PAA was to determine whether or not PAA breakdown products form affected the hideout return.

Table 4.4 shows the experimental matrix based on feed solution and porosity. The feed containing DI water only was used to confirm baseline condition in the reactor, and was performed between any two runs unless otherwise noted. This check ensured that the experiment was corrupted by residual amounts of chemicals remaining in the system from the previous run. Each type of solution was tested two times for statistical purposes except the DI + NaCl + PAA + ETA. More tests were performed on this feed solution to confirm the repeatability of the results. The porosity levels of 30% and 20% were chosen to facilitate comparisons with Coonradt's (1999) results.

4.3.3 Experimental Procedure

a. Start Up Procedure

The autoclave was initially filled with the test solution before putting lid back on the autoclave. Otherwise, it took several hours to mechanically pump in the solution. Before turning on the pump, the pump hydraulic fluid was checked. Then, the pump was turned on with the flow rate set to 20 mL/min to pump the feed solution into the system. A furnace was used to preheat the feed solution before entering the autoclave. This minimized the temperature difference between the solution in the autoclave and the solution right before entering the autoclave. In another words, this minimized the temperature fluctuation of bulk temperature

Table 4.4 The matrix of experimental test runs

Test Solution Types /Number of Test Runs	Packing Porosity	
	30 %	20%
Baseline run DI only	>5	>5
Baseline run DI + ETA	2	2
Baseline run DI + PAA	0	2
Baseline run DI + PAA + ETA	2	2
Baseline run DI+ baked PAA + ETA	2	0
Baseline run DI + 50% baked PAA + 50% PAA + ETA	0	2
Test run DI + NaCl + ETA	2	2
Test run DI + NaCl + PAA + ETA	4	4
Test run DI + NaCl + Baked PAA + ETA	2	0
Test run DI + NaCl + 50% baked PAA + 50% PAA + ETA	0	2
Total	~20	>20

in the autoclave. The pressure of the system was initially set to 400 psig. The bulk water temperature was elevated at a rate of 50 degrees F/hour (27.8 degrees C/hour) on both preheater and temperature controller of the autoclave. As the temperature of the bulk and feed solution reached 400 °F, which was very close to the saturation temperature of 400 psig, system pressure was elevated to the final pressure of 870 psig. Before adjusted the system pressure to 870 psig, system temperature (both preheater temperature and autoclave temperature) must be kept below 400 °F so that boiling would not occur in the autoclave and in the feed line. It was found by experience and discussion with in use together at Rockwell International that this method of reaching the desired temperature and pressure reduced system instability such as significant steam production. The system was allowed to reach steady state over a 24 hours period at which times the temperature and pressure data was analyzed to ensure steady state condition were reached. It was important that the crevice solution be saturated so that the heat transferred from heater tube was utilized entirely as superheat.

b. Procedure for Hideout and Return Process

Baseline information was manually recorded including passive temperature, active temperature, total conductivity, Na-specific conductivity, Cl-specific conductivity, and pH value from both meters and computer before turning on the heater tube. In order to prevent a short circuit, the procedure for turning on the heater tube was performed as follows. First, the heater tube was plugged in, and the

temperature controller was set as desired. Finally, turn the variac was turned up in increments of 50 watts over 3 minutes to get the desired heat flux of 150 watt. When the crevice heater tube was on, the hideout behavior started immediately. During the hideout period, the salt concentration dropped initially followed by a slow rise to reach its original concentration. The crevice heater tube was turned off when (and not before) the concentration of the salt rise back to its original value. The return period began when the heater tube was turned off. At the beginning of this return period, a sharp surge of salt concentration could be seen, followed by a slow decrease of salt concentration, and finally the original concentration was reached. The heater was turned off when the salt concentration reached the original feed value again. After each experiment, the system was flushed with de-ionized water for several hours to remove the residue solution until the DI baseline was reached. A checklist detailing the hideout and return processes is shown in Appendix B.

4.4 Data Analysis

Several variables were measured. From the measured data, other relevant information was calculated. Superheat was obtained from the difference of crevice solution temperature (T_{crevice}) and bulk water temperature (T_{bulk}). From the total conductivity data, the salt concentration was calculated from a calibration curve. The plot of salt concentration versus time gave us information about the salt hideout return behavior. The total amount of salt accumulated in the crevice when the heater tube was on or released from the crevice when the heater tube was off were

calculated by integrating the area under the curve. The plot of total mass accumulation versus time gave information about the accumulation rate. The measurement from both sodium and chloride specific probes tell if there was any preferential hideout during the experiment. The pH value was recorded throughout the experiment to monitor any pH change during the hideout return period, which gave information on preferential hideout.

5.0 Results and Discussion

5.1 Total Conductance Profile

Table 5.1 shows the experimental matrix that lists the order runs were completed. Total conductance was plotted versus time to construct the total conductance profile of each run.

5.1.1 DI Runs

DI runs with an original conductance of 0.085 micro-siemen and pH of 5.3 were performed to establish the system baseline. The typical total conductance profile of a DI run performed shows that the total conductance is essentially constant throughout the experiment. However, the enlarged total conductance profile of the DI run, Figure 5.1, shows a small opposite reaction of hideout and return, which is consisted with the results reported by Coonradt in 1999. This spike is noticed 50 minutes after turning on the heater tube, as shown in Figure 5.1, which is the mean residence time of the system. This spike has less than 0.1 micro-siemen (or less than 0.1 ppm), however, it is much smaller than Coonradt observed in his experiment,

Table 5.1 Experimental Matrix

Test Solution Types /Number of Test Runs	Packing Porosity	
	30 %	20%
July 16, 1999 DI only	✓	
July 26, 1999 DI + PAA + ETA	✓	
July 27, 1999 DI + PAA +ETA	✓	
July 28, 1999 DI + baked PAA + ETA	✓	
July 29, 1999 DI+ NaCl + PAA + ETA	✓	
July 30, 1999 DI+ baked PAA + ETA	✓	
July 31, 1999 DI+ NaCl + PAA + ETA	✓	
August 2, 1999 DI only	✓	
August 3, 1999 DI only	✓	
August 4, 1999 DI + ETA	✓	
August 5, 1999 DI + NaCl + ETA	✓	
August 6, 1999 DI + ETA	✓	
August 7, 1999 DI + NaCl + ETA	✓	

August 8, 1999 DI + NaCl + baked PAA + ETA	✓	
August 9, 1999 DI + NaCl + baked PAA + ETA	✓	
August 17, 1999 DI only		✓
August 17, 1999 DI only		✓
August 18, 1999 DI + NaCl + ETA		✓
August 19, 1999 DI + NaCl + ETA		✓
August 20, 1999 DI + NaCl + PAA + ETA		✓
August 21, 1999 DI + NaCl + PAA + ETA		✓
August 22, 1999 DI + NaCl + 50% baked PAA + 50% PAA + ETA		✓
August 24, 1999 DI + NaCl + 50% baked PAA + 50% PAA + ETA		✓
August 25, 1999 DI + PAA + ETA		✓
August 25, 1999 DI + PAA + ETA		✓
August 26, 1999 DI + 50% baked PAA + 50% PAA + ETA		✓
August 26, 1999 DI + 50% baked PAA + 50% PAA + ETA		✓
November 19, 1999 DI + PAA		✓
November 21, 1999 DI + ETA		✓
November 22, 1999 DI + ETA		✓

November 23, 1999 DI+ PAA		✓
November 25, 1999 DI + PAA + ETA		✓
November 25, 1999 DI + PAA + ETA		✓

which was a 1.4 ppm spike. This implies that the DI water purified by Barnstead water purification system has much less ions than the previous DI water that Coonradt had. Since all other DI plots were similar, the rest of the DI results are provided in Appendix D.

As discussed in Coonradt's thesis, opposite hideout return is due to the preferential hideout of Na^+ in the crevice after turning on the heater tube. Na^+ starts hiding out in the crevice after turning on the heater tube while Cl^- turns into HCl in the bulk. This leads to a large amount of H^+ and OH^- leaving from the exit stream. Since H^+ and OH^- have much higher specific conductance than Na^+ and Cl^- have, a small spike appears after heater tube was on. After heater tube was off, the total conductance drops slightly since Na^+ slowly release from the crevice and reforms H^+ and OH^- into H_2O . A corresponding peak in the pH plot at the exact time serves to confirm this phenomenon is occurring.

Figure 5.1 Enlarged total conductance profile of DI only run with 30% porosity on July 15, 1999

5.1.2 NaCl-Free Runs

Runs without NaCl includes DI+PAA runs, DI+baked PAA runs, DI+ETA runs, DI+PAA+ETA runs, DI+baked PAA+ETA runs (for 30% porosity only) and DI+50%baked PAA +50%PAA+ETA runs (for 20% porosity only). Addition of 10 ppm PAA into DI water brings the total conductivity up to 5 micro-siemen and makes the feed solution more acidic. A significant opposite hideout return reaction similar to the opposite reaction seen in DI runs can be observed from the total conductance profile of DI+PAA runs as shown in Figure 5.2. The rest of the graphical presentations are all provided in Appendix F as they are all similar to Figure 5.2.

In order to elevate the pH to the desired value of 9.8 to simulate the actual bulk water pH value in nuclear power plant, a significant amount of ETA was added into the feed solution. As expected, addition of ETA contributes a lot more than the addition of 10 ppm PAA to the total conductance. The amount of ETA added brings the total conductance of feed solution up to around 30 micro-siemen. DI+ETA runs also have the opposite of standard hideout return curve on their total conductance profile, which is, having a spike right after turning on the heater tube

Figure 5.2 Total conductance profile of DI+PAA with 20 % porosity on Nov. 19, 1999

and a dip after turning off the heater tube. A dramatic enhancement of the spike of more than 10 micro-siemen can be seen after turning on the heater tube, as shown in Figure 5.3. The higher spike results from higher concentration of OH^- releasing from the ETA.

A similar opposite hideout return effect with a spike after the heater tube is turned on occurred in all the runs with NaCl-free feed solution. A 25 micro-siemen spike was obtained after the heater tube was on in the total conductance profile of DI+PAA+ETA runs, while a 20 micro-siemen spike was obtained for DI+baked PAA+ETA runs. The spike is followed by a dip in total conductance after turning off the heater tube. Obviously, addition of any of ETA, PAA or baked PAA alone or together will cause the enhancement of the spike in total conductance profile after turning on the heater tube. Table 5.2 shows the average spike for each feed solution in terms of area under curve.

5.1.3 NaCl-Containing Runs

Figure 5.4 shows the typical total conductance profile of the runs containing NaCl with 30% carbon fiber packing porosity. The three different kinds of NaCl-

Figure 5.3 Total conductance profile of DI+ETA run with 30% on August 6, 1999

Table 5.2 Average spike of each feed solution in terms of area under the curve

Test Solution Types / average spike (micro-S*minute)	Packing Porosity	
	30 %	20%
DI only	0.58	0.53
DI + ETA	375	188
DI + PAA	N/A	25
DI + PAA + ETA	467	175
DI+ baked PAA + ETA	481	N/A
DI + 50% baked PAA + 50% PAA + ETA	N/A	0.91
DI + NaCl + ETA	265	82
DI + NaCl + PAA + ETA	105	93
DI + NaCl + Baked PAA + ETA	104	N/A
DI + NaCl + 50% baked PAA + 50% PAA + ETA	N/A	108

Figure 5.4 Total conductance profile of DI+NaCl+ETA run with 30% porosity on August 5, 1999

containing runs using 30% porosity are DI+NaCl+ETA runs, DI+NaCl+PAA+ETA runs and DI+NaCl+baked PAA+ETA runs. See Appendix D to N for individual profiles. All those runs showed similar hideout return curve comparable to that shown in Figure 5.4. The expected hideout phase right after turning on the heater tube and return phase after heater tube off can be observed from the total conductance profile chart. A spike also can be noticed 30 minutes after hideout phase starts for each run which is the mean residence time of the system. This spike probably results from the preferential hideout effect discussed in 5.1.1, which was shown in the NaCl-free total conductance profile previously discussed. No significant difference between the three different types of runs can be recognized from the total conductance profile charts.

DI+NaCl+baked PAA+ETA runs were substituted for DI+NaCl+50%PAA+50%bakedPAA+ETA runs in the NaCl-containing runs with 20% carbon fiber packing porosity. Obvious differences can be observed by comparing each total conductance profile. As shown in Figure 5.5, 5.6 and 5.7, DI+NaCl+ETA run, Figure 5.5, had a 2.5 micro-siemen dip at the minimum point during the hideout phase and its hideout phase lasted about 400 minutes while

Figure 5.5 Total conductance profile of DI+NaCl+ETA run with 20% porosity on August 19, 1999

Figure 5.6 Total conductance profile of DI+NaCl+PAA+ETA run with 20% porosity on August 20, 1999

Figure 5.7 Total conductance profile of DI+NaCl+50%PAA+50%bPAA+ETA run with 20% porosity on August 22, 1999

DI+NaCl+PAA+ETA run, Figure 5.6, and DI+NaCl+(50%)PAA+(50%)baked PAA+ETA run, Figure 5.7, has an higher minimum and shorter hideout phase. This indicates that salt accumulate more in DI+NaCl+ETA runs than in the other two runs. A spike appeared in the hideout phase which is probably due to preferential hideout can be seen for all the runs with 20% porosity. During the return phase, a typical surge can be seen right after turning off the heater tube since salt accumulated was slowly released from the crevice. In addition, there is a huge difference on the height of the surge between DI+NaCl+ETA run which has a 10 micro-siemen surge and DI+NaCl+PAA+ETA run which has a 5 micro-siemen surge during the return phase. This implies that more salt released from crevice in DI+NaCl+ETA run after heater tube was off than it in DI+NaCl+PAA+ETA run. A more detailed comparison is shown in Table 5.3. Additional figures of NaCl-containing runs with 20% porosity are provided in Appendix I, J and L.

5.2 Total Accumulation in the Crevice

The total conductance profile can provide some initial trends of the total

Table 5.3 Total conductance profile characterization of NaCl-containing runs with 20% porosity

Feed Solution	Hideout Phase		Return Phase	
	Time Lasted (min)	Dip Size (micro-S)	Time Lasted (min)	Surge Size (micro-S)
DI+NaCl+ETA	~380 min	~2.5 micro-S	~200 min	>10 micro-S
	~450 min	~4.5 micro-S	~200 min	>10 micro-S
DI+NaCl+PAA+ETA	<100 min	~2 micro-S	~150 min	<5 micro-S
	<100 min	~2 micro-S	~150 min	5 micro-S
DI+NaCl+50%PAA+	~320 min	~3 micro-S	~180 min	6.5 micro-S
50%baked PAA+ETA	~220 min	~4 micro-S	~120 min	8 micro-S

accumulation of NaCl. However, it is necessary to calculate out the exact amount of total accumulation in the crevice. The amount of total accumulation in the crevice was obtained by integrating the area above curve during the hideout phase and the area under curve during the return phase of a (mass/time) versus time graph. The term (mass/time) was calculated by the following formula:

$$\text{mass/time (mg/min)} = \text{concentration(mg/L)} * (\text{L}/1000\text{ml}) * \text{flow rate(ml/min)} \quad (3)$$

Integration of these areas was performed using Excel. The spike area was not included. All the results for 30% porosity and 20% porosity are shown in Table 5.4 and Table 5.5.

Three different feed solutions were tested with 30% and 20% packing porosity.

DI+NaCl+baked PAA+ETA runs were replaced with

DI+NaCl+50%PAA+50%bakedPAA+ETA runs in the tests using 20% packing porosity in order to avoid the possibility of over baking PAA. Error was calculated to verify the total accumulation difference between hideout and return phase.

Theoretically, the total accumulation of impurity in the crevice during the hideout phase should equal the total amount of impurity that released from the crevice during the return phase. That is, the error should be zero for the theoretical case.

However, if there is preferential hideout, this could not be true. Our data shows preferential hideout so an error greater than zero was always obtained. From Table 5.4 and Table 5.5, the error calculated varies from 0.6% to 9.1%, which is within the acceptable range. In previous studies, the hideout differences ran as high as 30% using the exact same simulator (Rogers, 1997). Balakrishnan (1991) experienced errors in the range of 50%. When adjusting out the difference between sets, the percent error was only 20%. Coonradt (1999) experienced an error of 22% and 8% between DI and NaCl runs of the same set for hideout and return. Consequently, the error of 0.6% to 9.1% is quite small compared with previous studies.

The total accumulation ratio of the runs with the addition of PAA/bPAA to DI+NaCl+ETA runs was calculated out in the table using the following equation:

$$\text{Total Accumulation Ratio} = (\text{Total Accumulation in runs with PAA/bPAA}) / (\text{Total Accumulation in DI+NaCl+ETA}) \quad (4)$$

where the total accumulation of DI+NaCl+ETA runs is viewed as a standard as well as a base.

The repeatability or reproducibility for each type of the solution is calculated

for both 20% and 30% porosity experiment as shown in Table 5.4 and 5.5.

Repeatability is for the same feed solution done consecutively, however, reproducibility is for the same feed solution done nonsequentially. 1% to 13% of error was obtained for reproducibility; 1% to 15% of error was obtained for repeatability. This reflects that our system has a pretty small error in reproducibility and repeatability.

Obviously, there is no significant difference of total accumulation between DI+NaCl+ETA runs and DI+NaCl+bPAA+ETA runs with 30% porosity. However, there is difference between DI+NaCl+ETA runs and DI+NaCl+PAA+ETA runs. DI+NaCl+PAA+ETA runs accumulated 77% of the impurity amount which DI+NaCl+ETA accumulated. Based on the list in Table 5.2, preferential hideout was seen in each solution. It is probable that ETA, PAA, and breakdown products of baked PAA engaged in the process of hideout return in the crevice. In another words, what accumulated was not essentially all NaCl, there might be some PAA and ETA that accumulated in the crevice too. Coonradt (1999) experienced the accumulation of ETA when he was running a DI+NaCl+PAA+ETA run followed by a DI only run. He found that the DI+NaCl+PAA+ETA run had an extremely high

Table 5.4 Total accumulation in the crevice for the NaCl-containing runs with 30% packing porosity (not including the spike in the hideout phase).

Feed Solution	Total Accumulation		Total Accumulation		Error	Average	Ratio
	Hideout Phase		Return Phase				
	Date	mg		mg	%		
DI+NaCl+ETA	Aug. 5	11.63		11.64	3.74	11.82	1
	Aug. 7	12.44		11.54			
	Average	12.04	Average	11.59			
Reproducibility		93.49%		99.14%			
DI+NaCl+baked	Aug. 8	11		10.51			
PAA+ETA	Aug. 9	11.88		11.48			
	Average	11.44	Average	11	3.85	11.22	0.95
Repeatability		92.59%		91.55%			
DI+NaCl+PAA+	July 29	10		8.64			
ETA	July 31	8.71		9.27			
	Average	9.36	Average	8.96	4.27	9.16	0.77
Reproducibility		87%		93.2%			

Table 5.5 Total accumulation in the crevice for the NaCl-containing runs with 20% packing porosity (not including the spike in the hideout phase).

Feed Solution	Total Accumulation Hideout Phase		Total Accumulation Return Phase		Error	Average	Ratio
	Date	mg		mg			
DI+NaCl+ETA	Aug. 18	14.36		13.8			
	Aug. 19	12.95		13.36			
	Average	13.66	Average	13.58	0.6	13.62	1
Repeatability		90.18%		96.81%			
DI+NaCl+50%	Aug. 24	8.63		9.16			
bakedPAA+50%	Aug. 22	8.04		9.18			
PAA+ETA	Average	8.34	Average	9.17	9.1	8.78	0.64
Repeatability		93.16%		99.78%			
DI+NaCl+PAA+ ETA	Aug. 20	5.40		4.9			
	Aug. 21	4.63		5.34			
	Average	5.02	Average	5.12	2.0	5.07	0.37
Repeatability		85.74%		91.76%			

level of NaCl accumulation and second DI run appeared to have large amounts of ETA in the accumulation curve. This could indicate that some of the ETA was trapped inside that crevice and release during the return of this run. This could also describe why the return was significant larger than the number of ions accumulated during the hideout phase for some cases.

A similar table was made for the results with 20% porosity shown in Table 5.3. Comparing the total accumulation of these runs, a significant reduction of total accumulation can be recognized from the runs with the addition of PAA / baked PAA. For DI+NaCl+PAA+ETA runs Table 5.3, 37% as much impurity accumulated as that of DI+NaCl+ETA runs accumulated. In another words, DI+NaCl+ETA runs accumulated more than twice amount of salt than DI+NaCl+PAA+ETA runs did. This indicates that addition of PAA results in less total accumulation in the crevice. As to the runs with 50% PAA and 50% baked PAA, they performed in between DI+NaCl+ETA runs and DI+NaCl+PAA+ETA runs since the 50% baked PAA have lost the characteristics of PAA. Since it has not been determined how the PAA effects the hideout return mechanism, any change on the structure of PAA might effect the hideout return very much. PAA is a high

molecular weight molecule. After baking, some of the PAA break their chain in different levels. Some other researchers proposed that baked PAA, with lower molecular weight, might reduce the accumulation. However, from the results shown in Table 5.3, PAA reduced more accumulation than baked PAA did. From Table 5.3, DI+NaCl+50%bPAA+50%PAA+ETA runs accumulated 64% of the impurity amount that DI+NaCl+ETA accumulated.

Two graphs, which show the weight of total accumulation in the crevice for 30% porosity and 20% porosity, are provided as shown in Figure 5.8 and Figure 5.9. All the runs show a similar concentration behavior in spite of the data scattering. Initially, salt accumulates at constant rate until the equilibrium weight was reached. The driving force that drives salts continues to accumulate in the crevice before saturation happens is the heat flux generated from the heater cartridge, which results in a temperature difference between the tube and the crevice. As salt accumulating, boiling point of the crevice solution elevated until the temperature of the tube equals the elevated temperature of the crevice solution. Since the driving force for the salt accumulation disappears after crevice solution saturated, no more salt accumulate in the crevice.

Figure 5.8 Weight of total accumulation in the crevice during hideout period with 30% porosity

Figure 5.9 Weight of total accumulation in the crevice during hideout period with 20% porosity

Significant reduction of total accumulation for DI+NaCl+PAA+ETA runs can be observed in both figures. From Figure 5.9, a time lag of 2-4 hours can be noted after heater tube was on for DI+NaCl+PAA+ETA runs with 20% porosity. This may be due to the effect of PAA retarding accumulation which also reduces the total accumulation. In term of surface tension and capillary pressure, during this 2-4 hours, PAA probably acts to help the vapor and liquid phase mix probably by reducing the surface tension and capillary pressure in the crevice. PAA, a polymer that also can be considered as a surfactant, might also reduce the total accumulation by lowering the surface tension and capillary pressure in the crevice. Lowering the capillary pressure will result in less circulation within the crevice which, finally, leads to less total accumulation in the crevice. Since it is difficult to measure the surface tension and capillary pressure in the crevice, the real mechanism of PAA on reducing the accumulation in the crevice have not been approved.

The rate of total accumulation can also be obtained using Excel adding- trend line function. Table 5.6 shows the summary of the rate for each salt containing runs. The theoretical maximum accumulation rate can be calculated by the following equation:

$$rate_{accumulation} = \frac{\pi DLQ''}{H_{fg}} C_b$$

Where

D = diameter of the Inconel tube

L = length of the Inconel tube that is surrounded by the crevice

Q'' = heat flux = heater power/surface area for heat flux

C_b = bulk concentration

H_{fg} = latent heat of evaporation

In our experiment, the surface area surrounded by the crevice is 18.65 cm², the heat flux is 6.5789 J/s cm², the bulk concentration is 25 ppm and the latent heat of evaporation is 1578 KJ/Kg. The theoretical accumulation rate calculated is 0.1166 mg/min, which is higher than the rate obtained from the curve fit. The hideout rate in this experiment is slightly lower than that reported by Mann and Castle (0.066-0.133 mg/min). This is probably due to the low porosity used in this experiment than in Mann and Castle's experiment (47%). From Table 5.6, it is obvious that

Table 5.6 Summary of the rate of total accumulation

	30 % porosity		20 %porosity	
	Rate (mg/min)	R square	Rate (mg/min)	R square
DI+NaCl+ETA	0.0617	0.982	0.0468	0.9922
	0.0533	0.98	0.0376	0.9947
DI+bPAA+NaCl+ETA	0.0698	0.9971	-----	-----
	0.0942	0.9978	-----	-----
DI+50%PAA+50%bPAA+ NaCl+ETA	-----	-----	0.0342	0.9892
	-----	-----	0.043	0.9825
DI+PAA+NaCl+ETA	0.0374	0.97	0.0134	0.9933
	0.0282	0.9879	0.0189	0.9919

the higher the porosity the higher the accumulation rate. It was also found that the DI+NaCl+ETA runs have almost the same accumulation rate as DI+bPAA+NaCl+ETA runs and DI+50%PAA+50%bPAA+NaCl+ETA runs have. This means the addition of baked PAA or 50%PAA and 50%bPAA does not effect the accumulation rate very much, compared to DI+NaCl+ETA. However, there is a significant reduction of the rate for DI+PAA+NaCl+ETA runs compared to DI+NaCl+ETA runs. This means the addition of PAA did reduce the rate of accumulation.

5.3 Effect of Carbon Fiber Packing Porosity

In this study, carbon fiber is used to simulate porous corrosion products that are present in a real crevice. Table 5.7 shows the summary of the effect of carbon fiber packing porosity on total accumulation for the runs. As expected, the carbon fiber packing porosity effected the amount of total accumulation in the crevice.

DI+NaCl+ETA runs with 20% porosity had 1.15 more total accumulation in the crevice than the runs performed with 30% porosity. Since lower porosity results in more flow restriction in the crevice, runs with 20% porosity accumulate more in the

crease. Lower packing porosity seems to enhance the performance of PAA. Less amount of impurity accumulated in the crevice for DI+NaCl+PAA+ETA runs with 20% porosity (5.07 mg) than the runs with 30% porosity (9.16 mg).

Table 5.7 Summary of the effect of packing porosity on total accumulation

	Average Total Accumulation (mg)	Average Total Accumulation (mg)	Ratio (30% to 20%)
Packing Porosity	30%	20%	
Feed Solution			
DI+NaCl+ETA	11.82	13.62	0.86
DI+NaCl+PAA+ETA	9.16	5.07	1.8

5.4 Temperature Profile

The temperature of cartridge heater, eutectic salt, heater tube wall, and bulk solution was measured by thermocouples and recorded by the data acquisition system every minute. The heater temperature resulting from a constant power of 150 W was about 700 °F, the eutectic salt temperature was kept constant at 660 °F and the bulk temperature in the autoclave was maintained at the temperature of 525

°F after turning on the heater tube. The three thermocouples were used to build up a temperature profile from the heater cartridge to the tube wall similar to that of Mann and Castle's experiments. Although Mann and Castle said "crevice temperature" throughout their report, they actually measured the tube wall temperature in their experiments. Since there were technical difficulties with measuring the temperature in the tiny crevice, thermocouples were soldered along the heater tube surface to measure the tube temperature in Mann and Castle's work. In our experiment, the thermocouples were soldered on the tube wall surrounding the heater tube so were close to the crevice than the thermocouples used in Mann and Castle's case. Thus, by monitoring the tube wall temperature, it is possible to determine the relative temperature behavior in the crevice when there is no steam blanketing happened in the crevice. When steam blanketing occurs in the crevice, it acts as an insulator to block heat transfer from tube wall to the crevice, and thus, the tube wall temperature no longer reflect the behavior of crevice temperature.

A plot of temperature measured from the thermocouples soldered on the heater tube wall versus time gives additional information on what is occurring on the tube wall. Figure 5.10 shows a typical temperature profile. After reaching steady state,

Figure 5.10 Temperature profile of crevice temperature at crevice location A, C and G (DI+NaCl+ETA)

all the thermocouples at each location read around 525 °F before turning on the heater tube. The heater tube wall temperature measured by three thermocouples at different positions in the tube wall does not increase significantly through the entire run, as seen in Figure 5.10. Since most of the runs shared similar temperature profiles, only one typical graph is shown here. The rest of the plots are shown in Appendix D to M.

According to the model proposed by Mann and Castle, the increase in the solute concentration in the crevice may elevate the boiling point of the crevice solution. If there is no steam blanketing, the tube wall temperature must be increased slowly since the tube wall temperature reflect crevice temperature which increased slowly due to the concentration effect.

Newton's cooling law can be applied to explain heat transfer and temperature change throughout the experiment. Newton's cooling law can be expressed as:

$$Q = hA(T_{\text{heater cartridge}} - T_{\text{tube wall}}) \quad [5]$$

where Q is the heater power from heater cartridge, h is heat transfer coefficient,

$T_{\text{heater cartridge}}$ is the temperature of heater cartridge and $T_{\text{tube wall}}$ is the temperature

measured by the thermocouples on the tube wall. During the concentration process,

heater power (Q) and cartridge heater temperature ($T_{\text{heater cartridge}}$) recorded from thermocouple is kept constant. Q/A is also constant after the system reaches steady state at each point, even though each point in the r direction has a different temperature since A varies as a function of r . Since the heat transfer coefficient (h) increases during the concentration process, tube temperature ($T_{\text{tube wall}}$) needs to increase to balance the equation.

A significant increase of tube wall temperature around the center of the crevice can be seen in Figure 5.11 when each of 3 DI+NaCl+PAA+ETA runs and 2 DI+NaCl+50%PAA+50% baked PAA+ETA runs were performed with 20 % carbon fiber packing porosity. The tube wall temperature at the center of the crevice measured by thermocouple C increased 5- 10 °F 200-300 minutes after turning on the heater tube while the cartridge heater temperature maintained as constant temperature during that time period. At the same time, the eutectic temperature increased about 5-10 °F indicating that the heat transfer efficiency decreased from tube wall to crevice. This implies that the steam blanketing occurred at the center of the crevice during that period of time. Once steam blanketing occurs in the crevice, water vapor replaces liquid water in the crevice. Since water vapor has a

Figure 5.11 Temperature profile of crevice temperature of DI+NaCl+PAA+ETA run with 20% porosity

poor heat transfer coefficient compared to that of liquid water, power generated from the heater core accumulates in the eutectic salt and will be unable to transfer to the crevice through the tube wall from the eutectic salt. This results in the elevation of eutectic salt temperature and also the elevation of the tube wall temperature. Since steam blanking in the crevice acts as an insulator, which insulates between the tube wall and the crevice, heat was unable to get transferred from tube wall to crevice during that period of time. A significant temperature drop of 10 °F at thermocouple C position was seen 400 minutes after turning on the heater tube. This implies that good heat transfer starts to happen from that time point, and heat started to be transferred from tube wall to crevice again.

Many researchers recognized that steam blanketing occurred in their studies. In 1991, Balakrishnan investigated steam blanketing by observing the crevice temperature measured by the thermocouples in the tube wall. As seen in Figure 2.5, the temperature profile plotted from the measurements indicates steam blanketing in the crevice since the tube wall temperature went up and crevice temperature went down after turning on the heater tube. Rogers (1997) recognized the steam blanketing through visual observation of temperature measurements. It was shown

that the crevice volume had been replaced by approximately one-third steam blanketing.

Compared to the steam blanketing information from Balakrishnan and Rogers, the case in our experiment is more complicated. Steam blanketing occurred several hours after turning on the heater tube and flushed out all the impurity that had accumulated in the crevice. This is probably more evidence to show the reduction of accumulation of impurity in the crevice by adding PAA into the feed solution. PAA might drive the steam blanketing occur several hours after turning on the heater tube and results in lowering the salt accumulation in the crevice compared with those runs without the addition of PAA. The effect of adding PAA on temperature profile can also be recognized here. Addition of PAA led to an inconsistent tube wall temperature profile. Initially, the tube wall temperature at the center of the crevice increased due to bad heat transfer such as the steam blanketing effect. Then followed by a drop due to good heat transfer.

5.5 Superheat

Superheat is defined as the difference of crevice temperature between bulk

temperature.

$$\text{Superheat} = \text{crevice temperature} - \text{bulk temperature} \quad [6]$$

From the result of the runs with 30% porosity, it appears that the superheat is pretty stable and constant for all the runs. The typical superheat graph for all the runs are shown in Figure 5.12. Three crevice temperature were measured at different positions along the wall so that three different sets of superheat curve were obtained. The average superheat value is about 15 °F with the higher superheat at the center of the crevice. No significant effect of the addition of NaCl, PAA, baked PAA and ETA on superheat can be seen from those superheat charts.

The superheat curve changed in the PAA-containing runs with 20% porosity as shown in Figure 5.13. Superheat at the center of the crevice began to increase slowly during the first 200-300 minutes, and then had a drop 400 minutes after turning on the heater tube, which had same behavior as in their temperature profile plot. As to the superheat behavior at both ends of the crevice, they show the same trend as performed in temperature profile too. It is an expected trend because superheat is calculated from the subtraction of bulk temperature from crevice temperature. Since bulk temperature keeps constant throughout the experiment,

Figure 5.12 Superheat versus time of DI+NaCl+ETA run with 20% porosity

Figure 5.13 Superheat versus time of DI+NaCl+PAA+ETA run with 20% porosity

the behavior of crevice temperature is absolutely the same as superheat. Table 5.8

shows the average superheat for each feed solution at thermocouple C.

Table 5.8 Average superheat for each feed solution at thermocouple C.

Feed Solution	Superheat (K)		Superheat (K)	
Porosity	30% porosity		20% porosity	
DI	17.54	Average = 17.21	17.09	Average = 16.84
	16.88	Error = 3.76%	16.59	Error = 2.92%
DI+ETA	13.49	Average = 11.85	12.73	Average = 12.18
	10.22	Error = 24.2	11.63	Error = 8.64%
DI+PAA			21.64	Average = 20.36
			19.08	Error = 11.9%
DI+PAA+ETA	13.78	Average = 12.74	11.83	Average = 12.09
	11.71	Error = 15.0%	12.35	Error = 4.2%
DI+bPAA+ETA	12.11	Average = 11.48		
	10.85	Error = 10.4%		
DI+50% baked			13.76	Average = 13.12
PAA+50%PAA+			12.49	Error = 9.2%
ETA				

DI+NaCl+ETA	18.18	Average = 17.22	17.59	Average = 17.51
	16.27	Error = 10.5%	17.43	Error = 0.9%
DI+NaCl+50% bakedPAA+50% PAA+ETA			17.99 17.56	Average = 17.77 Error = 2.395
DI+NaCl+bPAA +ETA	15.13 12.07	Average = 13.6 Error = 20.2%		
DI+NaCl+PAA+ ETA	15.36 21.89	Average = 18.62 Error = 29.8%	17.84 19.02	Average = 18.43 Error = 6.2%

6.0 Conclusions

The addition of PAA in the feed solution did effect on sodium chloride hideout in a simulated steam generator crevice. PAA decreases the total accumulation of impurity in the crevice and also the total accumulation rate. Besides, the addition of PAA did effect the crevice temperature profile and superheat in the crevice.

However, the addition of baked PAA did not effect on sodium chloride hideout.

The carbon fiber packing at two different levels of porosity results in different level of sodium chloride hideout. For DI+NaCl+ETA runs, the lower the carbon fiber packing porosity the higher the total accumulation. For DI+NaCl+ETA runs, the lower the porosity the lower the total accumulation.

7.0 Future Work

For the further work studies, the following three topics are stated. The first one is to study the effect of different concentration of PAA on sodium chloride hideout to see if more addition of PAA in the bulk solution results in less accumulation of sodium chloride in the crevice. The second topic is to study the effect of PAA on different crevice packing porosity and different packing materials. The last topic is related to the study of the effect of PAA on other impurity hideout in the crevice to see if the addition of PAA decreases the accumulation of other impurity besides NaCl in the crevice.

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Conductivity meter calibration curve for 2.5 - 10 ppm NaCl solutions

Conductivity meter calibration curve for 10- 100 ppm NaCl solutions

Checklist for Making DI+ 25 ppm NaCl +10 ppm (b)PAA + pH = 9.8 ETA solution

1. ☐ Wash feed tank with tap water and then rinse with DI water.
2. ☐ Make sure that the DI water is “good”. “Good” means the DI water has the pH of around 5-6 and the conductance of around zero.

Resistivity from Barnstead system: _____ Mega-ohm-cm
Micro-siemen

5. ☐ Mix NaCl solution well. Measure the total conductance of the solution.

Expected Conductance (μmho)	Real Conductance (μmho) (Meter A & Cell C)—Non-salt solution (Meter B & Cell C)—Salt solution

Calibration Curve:

Conductance(μmho)=0.4771* Salt conc.(ppm)+15.95 (2.5-10 ppm)

$$\text{Conductance}(\mu\text{mho}) = 1.019 * \text{Salt conc. (ppm)} + 10.63 \quad (10-100 \text{ ppm})$$

6. ☐ Add **4.7619g (actually _____g)** polyacrylic acids (10.5 wt %) liquid solution into the tank or **9.5238g (actually _____g)** baked polyacrylic acids (5.25 wt %) liquid solution into the tank. Rinse the container with the water from tank several times in order to reduce the polyacrylic acids remaining in the beaker as less as possible.

Expected Conductance (μmho) (Meter A & Cell C)	Real Conductance (μmho) (Meter A & Cell C)

7. ☐ Use micropipette to slowly add ETA (99.7%) to the tank until pH 9.7- 9.8 is reached using meter & probe B.
8. ☐ Mix well
9. ☐ Feed final solution to on-line monitoring system

	On-line meter	LabVIEW
Total conductance	(Meter A & Cell A) (Meter B & Cell B) _____ (μS)	(Meter A & Cell A) (Meter B & Cell B) _____ (μmho) _____ (ppm)
Na probe		
Cl probe		
pH	(Meter & Probe C)	(Meter & Probe C)

APPENDIX C

Inter-experiments Startup & Shutdown Checklist

Feed solution: DI+25 ppm NaCl + 10 ppm (b)PAA + (pH 9.8) ETA

Date: ____/____/____ Name: _____

1. ☐ Feed solution information

	on-line system (from last checklist- making solution)	On-line meter	LabVIEW
Total conductance	Meter A / A Meter B / B _____(μmho)	Meter A / A Meter B / B _____(μmho) _____(ppm)	Meter A / A Meter B / B _____(μmho) _____(ppm)
Na probe			
Cl probe			
PH	(Meter & Probe C)	(Meter & Probe C)	(Meter & Probe C)
Temperature			

2. ☐ Make sure that the system reaches the same value of conductance recorded from “make solution” checklist. That means reach the steady state.
3. ☐ Check other steady state conditions before turn on the crevice heater tube: bulk temperature should be at 525 degrees F, pressure should be at 871 psig
4. ☐ Record the information from LabVIEW and manually before turning on the heater tube. Fill out form 1 (upper part).
5. ☐ Turn on heater tube.
 - a. set “tube” temperature of controller to 1000F
 - b. switch on the variac to 120 V
 - c. adjust the variac to 150W
6. ☐ Check saturation of crevice. If saturated, the conductance should be the same as recorded in form1.
7. ☐ Fill out form 1(lower part) before turning off the heater tube.
8. ☐ Turn off heater tube.
 - a. Turn down the variac to zero.
 - b. Switch of the variac to “Off”
 - c. Set tube temperature of controller at 32F.
13. ☐ Check if the return phase is completed.
15. ☐ Switch to DI and create new file.

Conductance VS Time (Aug. 02, 1999) (DI only) (0.3 Porosity)

Conductance VS Time (Aug. 02, 1999) (DI only) (0.3 Porosity)

Temperature Profile Inside the Heater and at the Crevice Wall (Aug 02, 1999) (DI only) (0.3 Porosity)

Superheat VS Time (Aug. 02, 1999) (DI only) (0.3 Porosity)

Conductivity VS Time (August 03,1999) (DI only) (0.3 Porosity)

Conductivity VS Time (August 03, 1999) (DI only) (0.3 Porosity)

Temperature Profile Inside the Heater and at the Crevice Wall (Aug. 03, 1999) (DI only) (0.3 Porosity)

Superheat VS Time (Aug. 03, 1999) (DI only) (0.3 Porosity)

Conductance VS Time (Aug. 4, 1999) (DI+ETA) (0.3 Porosity)

Temperature Profile Inside the Heater and at the Crevice Wall (Aug. 4, 1999) (DI+ETA) (0.3 Porosity)

Superheat VS Time (Aug. 4, 1999) (DI+ETA) (0.3 Porosity)

Conductance VS Time (Aug. 6, 1999) (DI+ETA) (0.3 Porosity)

Temperature Profile Inside the Heater and at the Crevice Wall (Aug. 6, 1999) (DI+ETA) (0.3 Porosity)

Superheat VS Time (Aug. 6, 1999) (DI+ETA) (0.3 Porosity)

Total conductance profile (Nov 19, 1999) (DI+PAA) (0.2 Porosity)

Temperature profile inside heater tube and at the crevice (Nov 19, 1999) (DI+PAA) (0.2 Porosity)

Superheat VS Time (Nov 19, 1999) (DI+PAA) (0.2 Porosity)

Total conductance profile (Nov 23, 1999) (DI+PAA) (0.2 Porosity)

Temperature Profile inside Heater Tube and at the Crevice (Nov 23, 1999) (DI+PAA) (0.2 Porosity)

Superheat VS Time (Nov 23, 1999) (DI+PAA) (0.2 Porosity)

Conductance VS Time (July 25, 1999) (DI+PAA+ETA) (back to back) (0.3 Porosity)

Temperature Profile Inside the Heater and at the Crevice Wall (July 25, 1999) (DI+PAA+ETA)
(back to back) (0.3 Porosity)

Crevice Superheat (July 25, 1999) (DI+PAA+ETA) (back to back) (0.3 Porosity)

Conductivity VS Time (July 26, 1999) (DI+PAA+ETA) (back to back) (0.3 Porosity)

Temperature Profile Inside the Heater and at the Crevice Wall (July 26, 1999) (DI+PAA+ETA)
(back to back) (0.3 Porosity)

Superheat VS Time (July 26, 1999) (DI+PAA+ETA) (back to back) (0.3 Porosity)

Conductance VS Time (July 28, 1999) (DI+PAA+ETA) (0.3 Porosity)

Temperature Profile Inside Heater Tube and at Crevice Wall (July 28, 1999) (DI+bPAA+ETA) (0.3 Porosity)

Superheat VS Time (July 28, 1999) (DI+bPAA+ETA) (0.3 Porosity)

Conductance VS Time (July 30, 1999) (DI+bPAA+ETA) (0.3 Porosity)

Temperature Profile Inside Heater and at Tube Wall (July 30, 1999) (DI+bPAA+ETA) (0.3 Porosity)

Superheat VS Time (July 30, 1999) (DI+bPAA+ETA) (0.3 Porosity)

Conductance VS Time (Aug. 25, 1999) (DI+PAA+ETA) (0.2 Porosity)

Temperature Profile Inside Heater Tube and at the Crevice (Aug. 25, 1999) (DI+PAA+ETA) (0.2 Porosity)

Superheat VS Time (Aug. 25, 1999) (DI+PAA+ETA) (0.2 Porosity)

Conductance VS Time (Aug. 26, 1999) (DI+50%PAA+50%bPAA+ETA) (0.2 Porosity)

Temperature Profile Inside Heater Tube and at the Crevice (Aug. 26, 1999)
 (DI+50%PAA+50%bPAA+ETA) (0.2 Porosity)

Superheat VS Time (Aug. 26, 1999) (DI+50%PAA+50%bPAA+ETA) (0.2 Porosity)

Conductance VS Time (Aug 18, 1999) (DI+NaCl+ETA) (0.2 Porosity)

Temperature Profile Inside Heater Tube and at the Crevice (Aug. 18, 1999)
(DI+NaCl+ETA) (0.2 Porosity)

Superheat VS Time (Aug. 18, 1999) (DI+NaCl+ETA) (0.2 Porosity)

Conductance VS Time (Aug. 19, 1999) (DI+NaCl+ETA) (0.2 Porosity)

Temperature Profile Inside Heater Tube and at the Crevice (Aug. 19, 1999) (DI+NaCl+ETA) (0.2 Porosity)

Superheat VS Time (Aug. 19, 1999) (DI+NaCl+ETA) (0.2 Porosity)

Conductance VS Time (Aug. 5, 1999) (DI+NaCl+ETA) (0.3 Porosity)

Temperature Profile Inside the Heater and at the Crevice Wall (Aug. 5, 1999) (DI+NaCl+ETA)
(0.3 Porosity)

Superheat VS Time (Aug. 5, 1999) (DI+NaCl+ETA) (0.3 Porosity)

Conductance VS Time (Aug. 07, 1999) (DI+NaCl+ETA) (0.3 Porosity)

Temperature Profile Inside the Heater and at the Crevice Wall (Aug. 07, 1999) (DI+NaCl+ETA) (0.3 Porosity)

Superheat VS Time (Aug. 07, 1999) (DI+NaCl+ETA) (0.3 Porosity)

Conductance VS Time (Aug. 20, 1999) (DI+PAA+NaCl+ETA) (0.2 Porosity)

Temperature Profile Inside the Heater Tube and at the Crevice (Aug. 20, 1999)
(DI+PAA+ETA+NaCl) (0.2 Porosity)

Superheat VS Time (Aug. 20, 1999) (DI+PAA+ETA+NaCl) (0.2 Porosity)

Conductance VS Time (Aug. 21, 1999) (DI+ NaCl+PAA+ETA) (0.2 Porosity)

Temperature Profile Inside Heater Tube and at the Crevice (Aug. 21, 1999)
(DI+NaCl+PAA+ETA) (0.2 Porosity)

Superheat VS Time (Aug. 21, 1999) (DI+NaCl+PAA+ETA) (0.2 Porosity)

Conductance VS Time (July 29, 1999) (DI+ NaCl+PAA+ETA) (0.3 Porosity)

Temperature Profile Inside Heater Tube and at the Crevice (July 29, 1999) (
DI+NaCl+PAA+ETA) (0.3 Porosity)

Superheat VS Time (July 29, 1999) (DI+NaCl+PAA+ETA) (0.3 Porosity)

Conductance VS Time (July 31, 1999) (DI+NaCl+PAA+ETA) (0.3 Porosity)

Temperature Profile Inside Heater Tube and at the Crevice (July 31, 1999) (DI+NaCl+PAA+ETA)
(0.3 Porosity)

Superheat VS Time (July 31, 1999) (DI+NaCl+PAA+ETA) (0.3 Porosity)

Conductance VS Time (Aug 8, 1999) (DI+NaCl+bPAA+ETA) (0.3 Porosity)

Temperature Profile Inside the Heater and at the Crevice Wall (Aug. 8, 1999)
(DI+NaCl+bPAA+ETA) (0.3 Porosity)

Crevice Superheat VS Time (Aug 8, 1999) (DI+NaCl+bPAA+ETA) (0.3 Porosity)

Conductance VS Time (Aug. 9, 1999) (DI+NaCl+bPAA+ETA) (0.3 Porosity)

Temperature Profile Inside the Heater Tube and at the Crevice Wall (Aug. 9, 1999)
(DI+NaCl+bPAA+ETA) (0.3 Porosity)

Superheat VS Time (Aug 9, 1999) (DI+NaCl+bPAA+ETA) (0.3 Porosity)

Conductance VS Time (Aug. 22, 1999) (DI+NaCl+50%PAA+50%bPAA+ETA) (0.2 Porosity)

Temperature Profile Inside Heater Tube and at the Crevice (Aug. 22, 1999)
(DI+NaCl+50%PAA+50%bPAA+ETA) (0.2 Porosity)

Superheat VS Time (Aug. 22, 1999) (DI+NaCl+50%PAA+50%bPAA+ETA) (0.2 Porosity)

Conductance VS Time (Aug. 22, 1999) (DI+NaCl+50%PAA+50%bPAA+ETA) (0.2 Porosity)

Temperature Profile Inside Heater Tube and at the Crevice (Aug. 24, 1999)
(DI+NaCl+50%PAA+50%bPAA+ETA) (0.2 Porosity)

Superheat VS Time (Aug. 24, 1999) (DI+NaCl+50%PAA+50%bPAA+ETA) (0.2 Porosity)

APPENDIX N

A membrane electrode assembly system consists of the membrane, solution 1 and 2 of constant composition, and electrode 1 and 2 as shown in Figure N-1.

Electrode 1 is an external reference electrode that is in contact with solution 1 (sample solution). Electrode 2 and solution 2 are internal filling solution and internal reference electrode. The the indicator electrode produces the cell potential (emf) which is equal to the sum of all the electrical potential differences arising within the membrane electrode assembly.

$$E=E_O+E_J+E_M$$

where E_O represents a reference potential that depends on the system of reference electrodes but is completely independent of the sample solution. So, E_O should be constant at constant temperature. E_J measures the potential distribution generated by diffusion layers within the aqueous system on the sample side. For practical purpose, it is convenient to choose electrolyte combinations where $E_J \approx 0$. Then, the emf measured is directly from the membrane potential E_M (Morf and Simon, 1971).

Figure N-1 Schematic presentation of a membrane electrode assembly. (Source:W. E. Mort and W. Simon, *Ion-Selective Electrodes in Analytical Chemistry*, 1971, p. 215)

In an ion-selective liquid membrane electrode, ion-selective sites are interposed between a sample and reference solution, as shown schematically in Figure N-2. A typical model of liquid-membrane electrode is shown in Figure N-3.

The continuous nature of electrode measurement is extremely important in many monitoring applications. Gotoh *et al.* successfully mounted several electrodes in flow cuvettes to measure and record continuously the arterial-venous difference in blood gas and electrolytes. However, there are still some limiting factors in ion-selective electrode potentiometry. The major critical limiting factor in the use of ion-selective electrodes is response time. In general, ion-selective electrodes exhibit response times varying from a second to several minutes, depending on the type of electrode, concentration range and the direction and the magnitude of concentration range (Durst, 1971). At very low concentrations, it is necessary to wait for a period of time.

Some potential sources of trouble are summarized in Table N-1 by Durst in 1971. One of the potential sources of error is the interrupt of other components in

Figure N-2 Schematic diagram of an ion-selective electrode. (Source:W. E. Mort and W. Simon, Ion-Selective Electrodes in Analytical Chemistry, 1971, p. 267)

Figure N-3 A typical model of membrane electrode. (Source:W. E. Mort and W. Simon, Ion-Selective Electrodes in Analytical Chemistry, 1971, p. 212)

<p>A. pH/mV Meter</p> <ol style="list-style-type: none"> 1. Electronic malfunction 2. Input impedance 3. Calibration <p>B. Indicator Electrode</p> <ol style="list-style-type: none"> 1. Activity vs. concentration 2. Species 3. Ionic distribution 4. "Electrode" interferences 5. "Solution" interferences 6. Fouling 7. Water activity 8. Disease states 9. Static electricity 10. Storage 	<p>C. Reference Electrode</p> <ol style="list-style-type: none"> 1. Residual liquid junction 2. Salt-bridge concentration 3. Salt-bridge composition 4. Liquid-junction structure 5. Suspension effect 6. Streaming potential 7. Tip potential 8. Cells without transference 9. Increment techniques <p>D. Drift</p> <ol style="list-style-type: none"> 1. Parallel 2. Concentration dependent 3. Random <p>E. Standards</p> <ol style="list-style-type: none"> 1. Preparation 2. Dilution 3. Matrix 4. Operational scale 5. Range
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Table N-1 Sources of trouble in using ion-selective electrode. (Source:W. E. Mort and W. Simon, Ion-Selective Electrodes in Analytical Chemistry, 1971, p. 316)

the solution. It can not be emphasized enough that ion-selective electrodes respond only to the free ions in solution, and any solution component that affects the ionic activities will also affect the apparent ionic concentration.

The sources of error from ion-selective indicator electrodes must also be considered. The ions to be measured must be in a form to which the electrode is sensitive. That is, if the ions are not in a dissociated form, the indicator electrode will not sense them. Another important point is that the ion-selective electrode is not absolutely specific for one particular ion and will respond to other ions with varying degrees of sensitivity. The pH effect is very important too. Light studied the effect of pH on the fluoride electrode response in a solution of constant total fluoride concentration (Light, 1969). In solutions more alkaline than pH 8, the electrode shows the opposite type of interference in which the electrode indicates the apparent increase in the fluoride level. In this case, the hydroxyl ion acts as direct electrode interference. That is, the electrode senses the hydroxyl ion as if it were a fluoride ion and responds directly to its activity level. Finally, improper electrode storage may also be a source of electrode inaccuracy.