1999

PAA studies in a simulated steam generator crevice

Richard Scott Coonradt
San Jose State University

Follow this and additional works at: https://scholarworks.sjsu.edu/etd_theses

Recommended Citation

Coonradt, Richard Scott, "PAA studies in a simulated steam generator crevice" (1999). *Master's Theses*. 1865.

DOI: <https://doi.org/10.31979/etd.u2qw-k9gr>
https://scholarworks.sjsu.edu/etd_theses/1865

This Thesis is brought to you for free and open access by the Master's Theses and Graduate Research at SJSU ScholarWorks. It has been accepted for inclusion in Master's Theses by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI[®]

Bell & Howell Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

**PAA STUDIES 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 Requirement for the Degree

Master of Science

by

Richard Scott Coonradt

August 1999

UMI Number: 1396166

**Copyright 1999 by
Coonradt, Richard Scott**

All rights reserved.

**UMI Microform 1396166
Copyright 1999, by UMI Company. All rights reserved.**

**This microform edition is protected against unauthorized
copying under Title 17, United States Code.**

UMI
300 North Zeeb Road
Ann Arbor, MI 48103

© 1999

Richard Scott Coonradt

ALL RIGHTS RESERVED

APPROVED FOR THE DEPARTMENT OF CHEMICAL ENGINEERING

Dr. Melanie McNeil

Dr. Peter Millett, EPRI

Dr. Art Diaz

APPROVED FOR THE UNIVERSITY

ABSTRACT

PAA STUDIES IN A SIMULATED STEAM GENERATOR CREVICE

by Richard Scott Coonradt

This thesis studies the effect of corrosion in a simulated steam generator crevice. It examines how the addition of PAA to the feed stream effects the mass accumulation, effective diffusion coefficient and superheat inside the simulated steam generator crevice. The process of hideout and return was used to determine the mass accumulation of Sodium Chloride inside the crevice. The average superheat was unchanged by the addition of PAA to the feed stream. PAA did lower the average effective diffusion coefficient by 1.38 cm²/sec, which was outside the statistical calculated error of 0.85 cm²/sec. The addition of PAA did appear to increase the surface tension, but not enough to reduce the mass accumulations of NaCl in the crevice.

CONTENT

Abstract.....	iv
Content.....	v
List of Figures.....	viii
List of Tables.....	xi
1 Introduction.....	1
1.1 Basic PWR Operation.....	2
1.2 Steam Generator Corrosion Process	3
1.3 Corrosion Problem History	5
1.4 Current Corrosion Threat	7
1.5 Basic Steam Generator Simulator	8
2 Literature Survey and Review	12
3 Research objectives.....	31
3.1 Justification	31
3.2 Hypothesis.....	32
3.3 Objective	32
4 Experiment Design and procedures	33
4.1 Autoclave and Crevice Design	33
4.2 Flow Loop Design	35
4.3 Experimental Design.....	38

4.4	Measurement Equipment and Calibration.....	42
4.5	Crevice Packing.....	43
4.6	Experimental Procedure.....	44
5	Results And Discussion.....	49
5.1	Superheat.....	51
5.2	DI (Baseline)	54
5.3	DI and ETA	56
5.4	DI, ETA and PAA.....	60
5.5	DI and NaCl.....	65
5.6	DI, ETA, PAA and NaCl.....	69
5.7	Error and Repeatability	74
6	Conclusion.....	81
7	Future Work.....	83
	Nomenclature	84
	References.....	85
	Appendix A: Chemicals and Equipment	89
1.1	Chemicals.....	89
1.2	Equipment	89
	Appendix B: LABVIEW Virtual Instruments	91
•	Master Control VI.....	91
•	Input VI.....	91
•	Process VI	91

• Archive VI.....	91
• Display VI	91
Appendix C: Graphical Representation of Data	105
• Temperature Profiles.....	105
• Superheat Diagrams.....	105
• pH Diagrams.....	105
• NaCl Concentration Diagrams	105
Appendix D: Sample Calculations	172
• Trapezoidal Integration of the Hideout Data.....	172
• Trapezoidal Integration of the Return Data	172
• Diffusion rate calculations	172

LIST OF FIGURES

Figure 1.1. Schematic Diagram of a Pressurized Water Reactor (Peters, 1990).....	2
Figure 1.2. Internals of a Steam Generator (Pedersen, 1978).....	4
Figure 1.3. Summary of Corrosion Problems (Douglas, 1995).	6
Figure 1.4. Diagram of Heated Crevice (Balakrishnan, 1991).	9
Figure 1.5. Typical Hideout and Return Process (Mann and Castle, 1983).....	10
Figure 2.1. Diagram of Heater Crevice (Mann and Castle, 1983).....	12
Figure 2.2. Weight of Sodium Chloride in Crevice (Mann and Castle, 1983).....	13
Figure 2.3. Typical Surge in Outlet Concentration after Switching off the Crevice Heater (Mann and Castle, 1983).....	14
Figure 2.4. Schematic of Isothermal Capsule (Millett, 1989)	16
Figure 2.5. Isothermal Capsule Material Balance (Millett, 1989)	17
Figure 2.6. Effective Diffusion Coefficients for Sodium and Chloride in Non-Protective Magnetite (Millett, 1989)	19
Figure 2.7. Solute Release from Crevice (Balakrishnan, 1991)	22
Figure 2.8. Normal Temperature Distribution in a Carbon Fiber Packed Crevice (Balakrishnan, 1991).....	23

Figure 2.9. Steam Blanketing Temperature Distribution In a Carbon Powder Packed Crevice (Balakrishnan, 1991).....	25
Figure 2.10. Schematic of Fluid Element Transport Process (Millett and Fenton, 1990)	27
Figure 2.11. Crevice Pressure Distribution (Millett and Fenton, 1990).....	29
Figure 2.12. Comparison of Repeatability at 120 PPM NaCl Feed and 85 Watt Heater Power (Rogers, 1997)	30
Figure 4.1. Crevice Cage Assembly	34
Figure 4.2. System Flow Loop Schematic	37
Figure 5.1. Temperature Profile Inside the Heater and Crevice Wall with DI+NaCl Feed (Ran on 990212)	50
Figure 5.2. Crevice Superheat with DI+PAA+ETA+NaCl Feed (Ran on 990204)	51
Figure 5.3. Expanded Plot of NaCl Concentration with DI Feed (Ran on 990212)	55
Figure 5.4. Expanded Plot of Autoclave Exit pH with DI Feed (Ran on 990212)	56
Figure 5.5. Autoclave Exit pH with DI+ETA Feed (Ran on 990518)	58
Figure 5.6. NaCl Exit Concentration with DI+ETA Feed (Ran on 990518).....	59
Figure 5.7. Autoclave Exit pH with DI+PAA+ETA Feed (Ran on 990521)	61
Figure 5.8. NaCl Exit Concentration with DI+PAA+ETA Feed (Ran on 990521)	64

Figure 5.9. Autoclave Exit pH with DI+NaCl Feed (Ran on 990213).....	66
Figure 5.10. NaCl Exit Concentration with DI+NaCl Feed (Ran on 990213)	68
Figure 5.11. Autoclave Exit pH with DI+PAA+ETA+NaCl Feed (Ran on 990618)	70
Figure 5.12. NaCl Exit Concentration with DI+PAA+ETA+NaCl Feed (Ran on 990512).....	71
Figure 5.13. NaCl Exit Concentration with Back-to-Back DI+PAA+ETA+NaCl Feed (Ran on 990610).....	73
Figure 5.14. Run Chart for Hideout, Return and Diffusion Rate.....	75
Figure 5.15. Adjusted Run Chart for Hideout, Return and Diffusion Rates	76

LIST OF TABLES

Table 2.1. Hideout Return Rates and Maximum pH of Effluent during Return (Balakrishnan, 1991)	21
Table 4.1. Experiment Design Matrix	40
Table 4.2. Specific Conductance of Interest Ions	43
Table 4.3. Solution Type Run Matrix.....	47
Table 4.4. Typical Run Cycle at a Specific Porosity.....	48
Table 5.1. Manual Superheat Measurements at Heater On/Off.....	53
Table 5.2. Real and Adjusted Mass Accumulation and Diffusion Rates for Hideout and Return.....	63
Table 5.3. Error Between Hideout and Return Accumulation For Each Run	67
Table 5.4. Real and Adjusted Error for Hideout and Return Accumulation and Diffusion Rates.....	78

1 INTRODUCTION

Corrosion of steam generators plays a vital role in the performance and uptime of nuclear power plants. Every nuclear power plant uses steam generators to cool the reactor core. Corrosion inside these steam generators has been so severe that nuclear power plants were only lasting 8-10 years instead of an expected 40 years of service. The resulting early shutdowns and extended nuclear refueling outages can cost up to 1 million dollars per day. In 1976, over 25 nuclear power plants were required to shutdown and others experienced energy capacity losses as high as 8 percent. Fortunately, mainly through the efforts of EPRI, the number of power plant shutdowns has been reduced to four plants a year, with an average of only 2 percent capacity loss.

In the past, enormous amounts of money have been focused on increasing the life of PWR steam generators through plant repair and corrosion prevention. A "fix it" approach has been taken by finding better materials, improving repair techniques, reducing maintenance and installing new sophisticated steam generators. Very little effort has been devoted to determining and understanding the origin of the corrosion failures. However, within the last couple decades, steam generator simulators have been developed to understand the fundamental mechanisms that create the corrosion problems. In order to understand and appreciate the current corrosion problems, basic plant operation will be discussed.

1.1 Basic PWR Operation

The basic operation of a pressurized water reactor (PWR) steam generator is illustrated in Figure 1. A massive amount of heat is released in the reactor core from the fission reaction. Heat is carried away from the reactor core by water that is sent to the tube side of a shell and tube type steam generator. Typical nuclear power plants have three to four steam generators for a single reactor core. Water that is heated by the fission reaction is referred to as primary water. Primary water is kept at a high pressure (about 2000 psia) to avoid boiling and pumped at a high flow rate to keep the reactor core

Figure 1.1. Schematic Diagram of a Pressurized Water Reactor (Peters, 1990).

cool. Heated primary water from the reactor core is cooled by the steam generators. Steam generators cool the primary water by boiling water on the shell side of 15,000 to

30,000 tubes. The outside water is referred to as secondary water and is kept at a low enough pressure (about 1000 psia) to maintain constant boiling. The secondary steam is then sent to a turbine where electric energy is produced. Secondary steam is then converted back to a liquid by passing it through a condenser.

1.2 Steam Generator Corrosion Process

The 15,000 to 30,000 tubes in a steam generator are held up by support plates. Figure 1.2 shows the typical internals of a steam generator and different support plate structures. Each of the support plate structures has an annular crevice between the tube and support plate. These annular crevices have a poor ability to circulate fluid. After many years of operation, corrosion products from other parts of the steam cycle start to collect in the crevices (Cohen, 1980). These corrosion products create a network of pores that isolate impurities to localized regions. When heat is applied across the crevice, boiling and dryout occurs in the localized regions. Therefore, dissolved impurities in the water become concentrated a million-fold and precipitate out as solids. This highly concentrated environment produces aggressive corrosion of the tubes and support plates.

Figure 1.2. Internals of a Steam Generator (Pedersen, 1978).

1.3 Corrosion Problem History

EPRI has played a major role in virtually eliminating or successfully managing almost all forms of corrosion degradation in steam generators. EPRI has done this by recommending revolutionary methods of water chemistry control, secondary fluid filtration systems, low temperature long period fabrication techniques of the U-bend tube, and different support materials with grid-type designs. Figure 1.3 shows a summary of the corrosion problems and solutions found in steam generators. Most of the corrosion problems have been eliminated by water chemistry control. Water chemistry control programs have been around for years. Many of the programs have been very successful in eliminating problems and others have been linked to creating worse ones. A quick history of the water treatment programs will be discussed.

Water treatment in early days of steam generators was based on conventional methods used in fossil fuel plants. The conventional method was to use sodium phosphate in the secondary fluid to reduce corrosion; this led to aggressive corrosion and wastage of the Alloy 600 steam generator tubes from the formation of phosphoric acid and precipitates in the solution. Tube wastage was so severe in 1974 that over 7 steam generators had to be replaced after only 13 years instead of the expected 40 years (Douglas, 1995). Responding to these challenges, EPRI introduced the All Volatile

Figure 1.3. Summary of Corrosion Problems (Douglas, 1995).

Secondary Water Treatment (AVT) program (Millett, 1995).

The AVT program took a serious look at different water chemistry treatment methods. The AVT program recommended the use of hydrazine to remove oxygen out of the water and the use of ammonia to control the pH. This method was extremely effective in eliminating the tube wastage problem but resulted in tube denting. Tube

denting is caused from the corrosion of the carbon steel support plates. Since magnetite (Fe_3O_4) has twice the volume of the original carbon steel, the crevice is quickly filled and denting of the tube results from the vibration of the supports during operation. Ammonia caused rapid corrosion of the carbon steel support plates, which eventually squeezed and dented the tubes. In response to the tube denting problems, EPRI established the Secondary Water Chemistry Guidelines. The Secondary Water Chemistry Guidelines used boric acid treatment in the secondary water to reduce tube denting while still controlling pH.

1.4 Current Corrosion Threat

In the late 1980s, more pervasive types of tube degradation in PWR steam generators were encountered, intergranular attack (IGA) and intergranular stress corrosion cracking (IGSCC). IGA and IGSCC are corrosion that occurs between the grains of a substance, or along grain boundaries. IGA and IGSCC happen normally in two places, on the secondary side of the tubes near the support plates and in the tubesheet crevices at the bottom of the steam generator, as shown in Figure 1.3. IGSCC is predominantly found on the tubesheet ends because of the grain boundary defects created during manufacturing, when the ends of the tubes were expanded to fit snugly inside holes in the bottom tubesheet. To combat this new problem, EPRI established the Steam Generator Strategic Management Project.

EPRI and participating member utility companies established the Steam Generator Strategic Management Project (SGSMP) to develop a balanced package of

long-term and short-term options for addressing steam generator operation issues. The SGSMP determined a direct link between intergranular corrosion problems and pH. Significant reductions of IGA and IGSCC were obtained by sustaining a neutral pH balance in the secondary fluid. New aggressive water treatment processes have shown positive results, such as organic amines to reduce the transport of sludge buildup and complex acids to impose an even distribution of negatively and positively charged ions in crevices (Green, 1995).

1.5 Basic Steam Generator Simulator

Access to actual steam generator crevices has not been possible to date since it would be very difficult to position the proper measurement devices inside the crevice (Green, 1995). Therefore, experimental steam generator simulators have been developed to understand and study typical industry corrosion problems. Information gained by experimental studies has already been used to assist in water chemistry guidelines, recommend better steam generator designs and to develop models that predict steam generator life. Most of the steam generator simulators only replicate a single crevice of the type normally found in industry. A typical crevice steam generator simulator is shown in Figure 1.4, later discussed in more detail. Almost every simulator uses some sort of crevice packing to imitate normal crevice deposits that normally take years to accumulate. The crevice packing produces the highly aggressive corrosion environment present in industrial generators. The most common types of porous media used are;

carbon fiber, carbon power, diamond powder, zirconia, hematite, packed magnetite and grown magnetite.

Figure 1.4. Diagram of Heated Crevice (Balakrishnan, 1991).

Since it has not been possible to actively monitor the crevice chemistry in a steam generator, the method of hideout and return has been used. Hideout is when impurities accumulate in the crevice and return is when the impurities are released out of the crevice. Without a heat flux across the crevice there is no sodium chloride accumulation, as described in section 1.2, and the exit conductivity of the solution equals the

conductivity of the feed. When the heat flux is applied across the crevice the crevice begins to hideout or remove sodium chloride from the bulk solution resulting in a noticeable drop in the outlet salt concentration. Figure 1.5 shows a typical hideout and return process. Each impurity species will accumulate to an equilibrium concentration in the crevice. The corrosion process is directly related to the crevice solution concentration. The crevice solution concentration is severely limited by diffusion in the crevice. Diffusion is one of the most important processes that limit the buildup of impurities in the crevice (Millett, 1990).

Figure 1.5. Typical Hideout and Return Process (Mann and Castle, 1983).

Steam blanketing is another important phenomenon to understand when studying porosity and diffusion effects in a simulated crevice. Steam blanketing reduces the hideout efficiency of the crevice. The hideout efficiency is the difference between the observed and calculated hideout rates, the latter being the rate for 100 % efficient hideout. Steam blanketing is when the crevice fills with a steam bubble instead of with highly concentrated solutions. It causes the crevice to hideout less solute since many of the pores that isolate impurities are filled with steam. Since diffusion calculations assume complete wetting of the porous media, steam blanketing will cause errors in diffusion calculations.

2 LITERATURE SURVEY AND REVIEW

Mann and Castle constructed a small-scale simulator to study the hideout of nonvolatile salts in steam generator support plate crevices. Figure 2.1 shows the construction of the simulator. The design utilized a 1 liter autoclave that housed an electric heater to simulate the tube side heat flux and a low-carbon steel ring to mimic the support plate. A constant heat flux was maintained at the heater. The simulator was packed with carbon fibers (56 % porosity) and had a 0.3 mm wide crevice. The autoclave

Figure 2.1. Diagram of Heater Crevice (Mann and Castle, 1983)

was operated at 928 psi and 280°C to mimic normal steam generator operating conditions. Salt accumulation within the crevice was tested by passing different sodium chloride solutions at different crevice heat fluxes, results are shown in Figure 2.2.

Mann and Castle determined that concentration in the crevice is controlled by the amount of superheat available in the crevice. Superheat is defined as the excess

	FEED CONCENTRATION		HEATER POWER	
	mg/kg NaCl		Watts	Btu/ft ² hr
O	120		150	47.000
X	12		230	72.000
□	12		150	47.000
+	12		85	27.000
▲	1.2		150	47.000
▼	1.2		150	47.000

THE POINT MARKED ▼ WAS MEASURED AFTER PREVIOUSLY ESTABLISHING EQUILIBRIUM AT 120 mg/kg NaCl, 150 WATTS.

Figure 2.2. Weight of Sodium Chloride in Crevice (Mann and Castle, 1983)

temperature between the crevice heater wall and the saturation temperature of the bulk water solution. As illustrated in Figure 2.2, it is clear that the equilibrium weight of salt increased as the heater power (or available superheat within the crevice) increased. In fact, the storage weight of sodium chloride increased over 22 times (from 1 to 22 mg) by just increasing the heater power 2 times (from 27k to 47k btu/ft²hr). This figure also indicates that the equilibrium weight of salt in the crevice was only a weak function of the feed concentration. By increasing the feed concentration 100 times (from 1.2 to 120

Figure 2.3. Typical Surge in Outlet Concentration after Switching off the Crevice Heater (Mann and Castle, 1983)

mg/kg) the amount of sodium chloride only increased 2 times (from 6 to 15 mg). This is relatively small when compared to a 4 times (from 8 to 30 mg) increase of sodium chloride by changing the heater power only 1.5 times (230 to 150 Btu/ft² hr).

Figure 2.3 shows a typical salt release after the crevice heater was switched off. At first, a large surge of salt is released, then a steady release, and finally a trailing off period. The first surge of salt is caused by a release of salt from the mouth of the crevice and around the crevice heater. The steady release phase is the dominant portion of the return phase and is important because it represents the diffusion coefficient for the porous material in the crevice. Mann and Castle showed that the diffusion coefficient could be approximated by equation 2.1.

$$k = \pi D / 4 l^2 \quad \text{[Equation 2.1]}$$

Where,

k is the rate constant (1/s),
 D is the diffusion coefficient for the species (m²/s), and
 l is the diffusion path length, or half the depth of the crevice (m).

The rate constant (k) is determined from a slope of log concentration versus time. The rate constant is the slope of a straight line running through the experiment points using a Linear Regression method (Mann and Castle, 1983).

Millett used a different approach to measure the effective diffusion coefficients for concentrated salt solutions in a dented support plate crevice simulator. A dented support plate crevice simulator is one that produces tube denting from the intense

production of magnetite in the support plate crevice. Figure 2.4 shows a schematic of the isothermal capsule and carbon steel slug used to grow the magnetite.

Figure 2.4. Schematic of Isothermal Capsule (Millett, 1989)

Magnetite was grown by filling the capsule with an extremely aggressive corrosion solution at a pressure of 880 psig and temperature of 260°C. After a set number of days, the capsule was flushed with demineralized water until an apparent

steady-state conductivity level was reached. Once this condition was reached, measurements were taken to calculate the diffusion coefficient. The steady-state conductivity level was assumed to be from the diffusion of concentrated solution within the magnetite pores. This experiment was repeated with different denting solutions and operating temperatures.

Figure 2.5. Isothermal Capsule Material Balance (Millett, 1989)

The diffusion coefficient was calculated from a series of equations developed by Millett. Millett performed a material balance over the capsule as shown in Figure 2.5. From the material balance and some simplifying assumptions, Millett showed that the diffusion coefficient could be calculated from equation 2.2.

$$D_e = 2QC_c b / SC_{avg} \quad \text{[Equation 2.2]}$$

Where,

Q is the capsule feed rate,
 C_c is the capsule concentration,
 b is $\frac{1}{2}$ the slug thickness,
 S is the surface area available for diffusion,
 C_{avg} is the average pore concentration $(C_{y=0} + C_c)/2$.

All of the variables can be directly measured or determined by examining the porous packing material. Millett calculated the individual diffusion coefficients for sodium and chloride over a wide range of temperatures, shown in Figure 2.6. This figure shows that the effective diffusion coefficient for sodium and chloride at 274 °C (525 °F) should be around 1.0×10^6 and 4.0×10^6 cm²/sec, respectively.

Balakrishnan constructed another simulator similar to Mann and Castle's to test complex mixtures of feed water impurities. Mixtures of sodium chloride, sodium sulfate, and calcium chloride were studied in crevices packed with carbon fiber or carbon powder. Figure 1.4 shows the schematic diagram of the autoclave. The autoclave was operated at 272 °C and at a saturation pressure of 863 psia. The heater tube was fabricated from alloy 600 and the support plate was made from 405 stainless steel. The autoclave had a system volume of 0.15 L with a crevice gap of 0.3 mm. Three thermocouples (iron-constantan) were placed at different elevations in the heated zone to monitor the tube temperature. Three thermocouples were also placed at different heights in the collar, with the tips as close to the crevice wall as possible, to measure the crevice temperature.

Figure 2.6. Effective Diffusion Coefficients for Sodium and Chloride in Non-Protective Magnetite (Millett, 1989)

Balakrishnan found that the superheat produced from a carbon powder-packed crevice was higher than for a carbon fiber-packed crevice. Although the porosity of both packings were the same (45%), the carbon powder-packed crevices only required a heat flux of 150 kW/m^2 , whereas the carbon fiber-packed crevices required 250 kW/m^2 to obtain the same amount of superheat (50°C). The accumulation rate of impurities was also greater for the carbon fiber-packed crevice compared with the powder-packed crevice. These results let to several important conclusions about porous materials in the crevice.

- Fiber packing have their pores lined up parallel to the axis of the heater or circumferentially along the heater making all the pores inter-connected, while powder

packing have their pores randomly distributed, many of them isolated and unavailable for solute accumulation.

- The random distribution of powder packing voids creates a higher-pressure drop in the packing. This higher-pressure drop in the packing resists the capillary flow (discussed later) of solution into the crevice.
- Most of the powder packing voids are filled with steam, thus, not taking part in the heat transfer process or in the accumulation of concentrated solutions.
- Some of the heat flux will be conducted away from the crevice area and not transferred to the solution as assumed and calculated for powder-packed crevices.
- Packing materials with a high thermal conductivity could cause an even greater decrease in the crevice efficiency.

Balakrishnan found that steam blanketing had a direct impact on his diffusion coefficient calculations. When steam blanketing was detected from the temperature profile, the diffusion path length in the crevice will be much smaller than half the crevice length due to the steam bubble. This leads to diffusion coefficient calculations that are too high. Table 2.1 shows a variety of hideout returns when using different hideout times in carbon powder-packed crevices. The short-term tests were considered 28 through 35,

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	0.36			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

Table 2.1. Hideout Return Rates and Maximum pH of Effluent during Return (Balakrishnan, 1991)

and the long-term tests were 41 through 55. What he found was that for the short-term tests, the solute accumulation was near the mouth of the crevice and did not penetrate into the center. After an average value of all the short term measurements were taken, the diffusion coefficient calculations were off by more than 45 % when using the standard diffusion path length. For the long-term tests, the salt had enough time to fully penetrate the crevice and calculations were within 15 % when ignoring precipitation effects. Balakrishnan used equation 2.1, developed by Mann and Castle, to determine diffusion coefficients. Figure 2.7 represents a steady return phase and linear regression line from

Figure 2.7. Solute Release from Crevice (Balakrishnan, 1991)

one of Balakrishnan's crevice simulator experiment runs. From a similar test run, the diffusion coefficient was calculated to be $1.4 \times 10^{-8} \text{ m}^2/\text{s}$. This compared very close with Lindsay's estimated sodium chloride diffusion coefficient of $2.26 \times 10^{-8} \text{ m}^2/\text{s}$ at 275°C , which gives $1.0 \times 10^{-8} \text{ m}^2/\text{s}$ when considering a porosity of 45% (Lindsay, 1981).

Many other researchers have experienced decreased hideout efficiencies from steam blanketing. Mann and Castle experienced reduced efficiencies as low as 20 % with corrosion filled fiber packing (Mann and Castle, 1987). Other workers have found reduced efficiencies in the range of 46 % when using tightly packed synthetic and natural magnetite's (Cleary et al., 1983).

Figure 2.8. Normal Temperature Distribution in a Carbon Fiber Packed Crevice (Balakrishnan, 1991)

Balakrishnan showed that steam blanketing could be detected by examining the temperature profiles of thermocouples in the crevice. As mentioned before, Balakrishnan used three thermocouples in the collar to measure the crevice temperature. For normal operation, all temperatures in the crevice should increase with time. Figure 2.8 illustrates how the temperature of each thermocouple should change with time.

For each of the thermocouples, the superheat increases with time. For the middle thermocouple, the available superheat increased from 50 °F to 66 °F. As the salt concentration builds up in the crevice, the saturation temperature (T_{sat}) will increase and the heat transfer coefficient (h) will decrease slightly for the liquid. For this constant heat

flux experiment (q''), the temperature at the surface will increase in order to maintain a heat balance, Newton's law of cooling (Munson et al., 1990).

$$q'' = h(T_{sat} - T_s) \quad \text{[Equation 2.3]}$$

The temperature at the center of the crevice increases to a maximum with the temperature of the top and bottom following after. This temperature distribution also confirms Mann and Castle's theory, that the solute first accumulating deep within the crevice, and then slowly spreading out into the rest of the crevice.

When the temperature at the center of the crevice decreases instead of increases, steam blanketing is responsible (Mann and Castle, 1987). Figure 2.9 shows a typical thermocouple temperature distribution for a carbon powder packed crevice that experienced steam blanketing. The temperature at the center of the crevice decreased by

Figure 2.9. Steam Blanketing Temperature Distribution In a Carbon Powder Packed Crevice (Balakrishnan, 1991).

27 °F as the hideout proceeded. From Newton's law, the only way for the temperature to decrease in the heart of the crevice it to have the heat transfer coefficient reduced since all other parameters remain unchanged. This type of behavior is possible if the crevice was initially steam blanketed but then filled with solution slowly as the hideout process continues. Other researchers have found similar observations when studying simulated corroded crevices (Baum et al., 1986).

Balakrishnan also proved that the steady phase of the return cycle is diffusion controlled. Balakrishnan explains that if all the solute in the crevice were released instantaneously after the superheat was removed, the slope of the steady decay would have been much larger. With a larger slope, the return rate would have been much faster.

From his simulated crevice, he calculated a first order half-time of about three minutes instead of the three hours that it took to diffuse. The initial surge of salt can be considered first order kinetics but the steady release is definitely diffusion controlled.

Researchers have developed theories to describe the morphology of fluid elements as they pass through porous deposits. Figure 2.10 shows the fluid element transport processes through a pore network (Millett et al., 1990). A pore network is a packed crevice, sludge, or porous deposit. As the liquid element moves through the pore, nucleate boiling occurs at the wall and the liquid mass decreases. In most cases, the impurity mass will decrease slower than the total liquid mass, thus causing an increase in the element concentration. The rate at which the concentration increases influences the heat, mass and momentum transport processes. The local heat transfer rate decreases since the saturation temperature of the pore solution will increase. As the element continues through the pore network, the liquid flux becomes insufficient to sustain nucleate boiling and “dryout” or film boiling occurs.

The element velocity is controlled by the capillary pressure in the crevice. Figure 2.11 shows that the bulk water is drawn into the pore network by a pressure gradient. The pressure gradient results from the countercurrent flow of liquid and vapor in the crevice. This means that the vapor pressure will be at a maximum at the bottom of the crevice and the liquid pressure will be at a minimum. The difference of the liquid and vapor phase within the pore is the capillary pressure. Since the capillary pressure is at a maximum at the bottom of the pore the liquid is forced into smaller and deeper pores.

Figure 2.10. Schematic of Fluid Element Transport Process (Millet and Fenton, 1990)

With high capillary forces, the liquid and vapor phases will flow in completely separate pores. Since the fluid and vapor transport in separate pores, the result is an extremely high concentration process in the liquid phase. The orientation of the crevices themselves have very little influence, since capillary forces dominate over gravitational and viscous forces for porous media's.

A study of the tubesheet crevice with different packing materials was performed (Campan and Shoemaker, 1988). The result was that carbon fiber packing was the most porous (0.5 – 0.6) and had the highest permeability. In tube support plate crevice testing, the liquid was found to penetrate the entire depth of the support plate, and that nucleate boiling was maintained throughout the carbon fiber packed crevice. Packed magnetite had a lower porosity (0.36) and permeability than carbon fiber. It was found that insufficient liquid was available to maintain nucleate boiling throughout the entire depth of tube support plate crevices. Consolidated magnetite with an even lower porosity (0.20-0.36) and permeability was found to penetrate the smallest depth in the tubesheet crevice.

All of the packed crevice research done to date has had difficulty with repeatability. Rogers ran two different sets of test for repeatability using a small-scale simulator similar to the one that was used by Mann and Castle. One set was run at a heater power of 85 watts, 120 ppm sodium chloride and another was run at 150 watts, 60 ppm feed concentration. For the first set, a difference of 12 % was calculated between

Figure 2.11. Crevice Pressure Distribution (Millett and Fenton, 1990).

the return mass for the two runs (Figure 2.12). For the second set, a difference of 30% was calculated. Other researchers experienced errors as high as 45 and 50% (Mann and Castle, 1983; Balakrishnan, 1991). Figure 2.12 also shows that hideout and return behavior was erratic but repeatable (Rogers, 1997). Packed crevices are very difficult to pack identically every time. Even when extreme care is taken, the density will be different for each run (Cleary et al., 1983). For long-term experiments, solid species start to precipitate out and effect the distribution of flow channels in the porous material. Even for short runs, the density can change due to compaction fluctuations within the crevice due to boiling within the pores (Brunet and Campan, 1987).

Figure 2.12. Comparison of Repeatability at 120 PPM NaCl Feed and 85 Watt Heater Power (Rogers, 1997)

3 RESEARCH OBJECTIVES

3.1 Justification

Corrosion problems with steam generators have been the major source of forced outages and capacity factor losses in the nuclear power industry. It has been estimated that plant repairs and lower plant power outputs have cost over 1.8 billion dollars in the last decade (Green, 1987). This is astronomical especially considering a steam generator design life of 50 years and the extensive research done over the last 20 years to reduce corrosion problems. EPRI has made some significant improvement in managing many types of corrosion problems. Many of the simple forms of corrosion have been eliminated through water chemistry control. Unfortunately, these methods have uncovered the more complicated corrosion problems, IGA and IGSCC. According to Douglas (1995), IGA and IGSCC could limit the life of even newer steam generators to 20-25 years. Today, the primary goal is to understand the principle mechanisms that create intergranular attack and stress corrosion cracking and to find water chemistry solutions to stop it.

3.2 Hypothesis

Addition of PAA in NaCl solutions will decrease mass accumulation in the simulated steam generator crevice compared to PAA-free NaCl solutions.

3.3 Objective

The main objectives of this research are to study the effect of PAA addition on the mass accumulation of NaCl into a simulated steam generator crevice. Rockwell International constructed the simulated steam generator crevice. PAA is a rheology modifier that may considerably increase the surface tension in the crevice, and thus reduce the amount of concentration buildup. Standard simulator tests will indicate whether favorable surface tension changes are sufficient to warrant testing in industrial settings. Simulator tests are designed to study the following objectives:

- The effect of PAA on the mass accumulation of NaCl in the crevice.
- The effect of PAA on the diffusion rate of NaCl out of the crevice.
- The effect of PAA on steam blanketing in the crevice.
- The effect of PAA on the superheat in the system.

4 EXPERIMENT DESIGN AND PROCEDURES

The heart of the experiment is an autoclave designed by Rockwell International after the one used by Mann and Castle. The autoclave simulates the secondary side of an industrial steam generator. There are many components required to bring the autoclave up to operating conditions and to study the effects inside the autoclave crevice. The autoclave and crevice design will be discussed first and then the overall support system will be described.

4.1 Autoclave and Crevice Design

The autoclave was fabricated from Inconel 718 and provides a system volume of 1 liter. The autoclave resembles a big pressure cooker except that the lid holds a heater tube that extends almost the entire length of the autoclave. A single Inconel 600 tube simulates a single tube located inside a steam generator. The heater tube, as shown in Figure 4.1, houses a 600 watt cartridge heater surrounded by eutectic salt consisting of 54.3 % KNO_3 and 45.7% NaNO_3 to enhance heat transfer to the tube wall. The heater extends 2.3 cm above and below the crevice ring to uniformly heat the crevice. Two separate K type thermocouples are located inside the cartridge heater to measure the simulated primary water temperature. Nine additional K type thermocouples have been welded to the wall of the tube to measure the crevice temperature, shown in Figure 4.1. The thermocouples were welded in a spiral fashion down the entire length of the crevice

Figure 4.1. Crevice Cage Assembly

and are 45° apart. The crevice temperature profile will be used to detect steam blanketing and calculate the amount of available superheat in the autoclave.

The crevice assembly consists of three main sections and is made from Inconel 718. The center section is the crevice ring and is supported by the top and bottom sections. The crevice ring can be separated into two halves to allow for easy access into the crevice after a simulator run. The crevice formed between the crevice ring and the tube is 0.24 mm. The crevice length is 30.5 mm, for a total crevice volume of 447 mm³.

Four stainless steel bolts are used on each support ring to securely fasten the crevice ring. The top and bottom support rings also have an upper and lower seal support ring attached with eight offset 316 stainless steel bolts. Figure 4.1 illustrates that within each of the seal support rings, a round Teflon washer is used to provide two critical functions. When the system is at operating conditions the round Teflon washers swell, and form an effective seal keeping fluid out of the crevices formed by the support rings. The other critical function served by the rings is that by swelling they straighten out the cage assembly and the center crevice. This ensures a uniform concentric crevice between the tube and crevice support ring. If the crevice is not uniform, or eccentric, impurities will concentrate with efficiencies as high as 19% (Balakrishnan, 1991).

4.2 Flow Loop Design

The equipment used in this project is shown schematically in Figure 4.2. A metering pump (Pulsa-Feeder) sends the test solution from a 50 gallon Nalgene feed tank,

located under a hood, through the system at 20 ml/min. Nitrogen is bubbled up through the feed tank to reduce the amount of dissolved oxygen present in the system so effects of corrosion from mechanisms not under study in this experiment will be reduced.

Metering pumps produce small, even fluctuations in pressure from the reciprocating action of the piston. Figure 4.2 shows a pulse dampener after the metering pump to reduce the pressure fluctuations. The pulse dampener was made from 30 feet of 1/16 inch PEEK (Poly/Ether/Ether/Ketone) tubing with a pressure rating of 3000 psia. A check valve with a pressure rating of 2000 psia was installed to protect the system from reverse flow in the event of pump or power failure. Plug valves are installed on each side of the autoclave to isolate it if necessary.

Before the solution enters the autoclave it is heated to 430 °F (221 °C). Figure 4.2 shows that the system uses an HP 5790 gas chromatograph oven to heat the solution. The feed stream flows through a coil of tubing inside the HP gas chromatograph oven operating at 475 °F (246 °C). Once the feed stream is heated the majority of the way from the gas chromatograph it enters the autoclave entrance.

Figure 4.2. System Flow Loop Schematic

The solution enters the autoclave through a fitting located approximately 1 inch from the bottom and exits ½ inch from the top. The internal volume of the autoclave will simulate the secondary side of a steam generator. Three Omega resistance band heaters blanket the autoclave to maintain the bulk water solution at a constant temperature. Two of the band heaters are rated at 500 Watts and one is rated at 250 Watts. Fuji Electric temperature controllers control all of the band heaters.

The exiting solution flows through a large tap water heat exchanger where it is cooled to 75°F (24°C). For safety precautions, a pressure relief valve will open if the system pressure ever reaches 1200 psia. As shown in Figure 4.2, a Grove backpressure regulator with a maximum operating range of 1000 psia, is used to maintain the system pressure at 870 psig. After exiting the back pressure regulator, the fluid is sent through a standard low flow rotometer, for determining the flow rate, and a Cole-Parmer conductivity meter, for determining the concentration in the test solution. Discharged fluid is then sent to a 25 gallon Nalgene exit tank located under a hood. The entire system utilizes ¼ inch 316 stainless steel tubing with a 0.035 inch wall thickness.

4.3 Experimental Design

The objective of the experiments is to determine the effect that PAA has when added to the secondary water of a simulated steam generator system. Two main aspects will be investigated. First the change in superheat will be observed and second the mass accumulation of NaCl in the crevice. Table 4.1 shows a classical experiment design matrix that lists a summary of the factors and response that will be studied. One main

factor will be changed during the simulator runs: solution type. The order in which this factor will be changed during the actual simulator runs will be discussed in more detail in section 4.6. This section only describes the expected responses that should be measured.

The temperature, pressure and crevice tube heater power will be held constant at 525 °F, 870 psig and 150 Watts, respectively. A crevice porosity level of 30% was selected and achieved as will be described later, as shown in Table 4.1. A set of runs is defined as all of the runs during the time that the simulator remains at operating conditions. If for any reason the simulator is brought down to atmospheric conditions, the next batch of runs performed after the simulator was brought back to operating conditions would be considered another set. This was done because the response variables changed considerably between sets. During analysis of data, error and repeatability will be considered by blocking out the differences between sets.

Factors are the independent variables that will be changed during this study. Response variables are the dependent variables that should react to different levels of the factor. Four key response variables were selected as shown in Table 4.1. Superheat is the most critical to EPRI, because it determines how much energy the steam generator produces. The addition of PAA should not decrease the amount of superheat in the system. In the power industry, any loss of power is unacceptable even if steam generator life increases. Superheat will be calculated by subtracting the bulk water temperature from the average crevice temperature in the autoclave.

Table 4.1. Experiment Design Matrix

	Factors Under Study	Levels
1	Solution type NaCl – 60 ppm PAA – 8 ppm ETA – To 9.8 pH	Baseline (DI) Type 1 (DI, ETA) Type 2 (DI, ETA, PAA) Type 3 (DI, NaCl) Type 4 (DI, ETA, PAA, NaCl)

	Response Variables	Measurement Technique
1	Superheat	Calculated from $T_{\text{crevice}} - T_{\text{bulk}}$
2	Equilibrium weight of NaCl in the crevice	Calculated from the rate of NaCl accumulation
3	Effective diffusion of NaCl out of the crevice	Calculated from the slope of log concentration versus time.
4	Steam blanketing	Crevice temperature profile characteristics

	Background Variables	Method Of Control
1	Packing porosity (Void Fraction)	30 %
2	Crevice heater power	Held constant at 150 Watts by power controller
3	Temperature in the bulk solution	Held constant at 525 °F by temperature control
4	Pressure in the system	Held constant at 870 psig by a pressure regulator
5	Error voltage from connection points	Subtracted out through CJC thermocouples

The NaCl exit concentration values will be obtained by converting specific conductance into NaCl concentration using a calibration curve created from 3 standard concentrations of NaCl. NaCl concentration values (i.e., converted specific conductance) in this report could be more than just NaCl ions. Ions from DI, ETA and PAA can alter the total conductivity and will be reported as NaCl under the method used in this study. Most of the simulator studies have used NaCl concentration to categorize hideout and

return even though other impurities are always present. All of the graphs in this report are kept in the NaCl concentration form to show how ETA and PAA effects the NaCl hideout and return results. The equilibrium weight of NaCl accumulated in the crevice will be calculated by integrating the area under the accumulation curve of (mass/time) versus time. The term (mass/time) was calculated by using the following formula.

$$\left(conc. \frac{mg}{L} \right) \left(\frac{1L}{1000ml} \right) \left(\frac{20ml}{min} \right) \quad [Equation 4.1]$$

The integration of these areas was performed using the trapezoidal method with Mathematica. Sample calculations will be provided in Appendix D.

It is expected that the equilibrium weight of NaCl will decrease by adding PAA. PAA increases the surface tension in the crevice. Increased surface tension, increases the capillary pressure in the crevice, and might result in a reduced amount of NaCl hideout. Since PAA increases the surface tension, it might also decrease the effective diffusion, or rate at which ions diffuse out of the crevice, during the return phase. Effective diffusion will be calculated from equation 2.1, which was derived by Mann and Castle (1983).

Steam blanketing will be identified by visual inspection of the temperature profile in the crevice. When steam blanketing occurs, the temperature will be at a maximum in the center of the crevice and decrease in an outward radial direction. It is expected that the equilibrium weight of NaCl will decrease with the presence of steam blanketing.

4.4 Measurement Equipment and Calibration

A National Instruments data acquisition system will be used to archive the pressure, concentration, pH and temperatures sensors. The system uses an AT-MIO-16 data acquisition card with two external modules in an SCXI-1000 chassis. The SCXI-1000 chassis houses an SCXI-1120 and an SCXI-1300. All of the type K thermocouples were connected to the SCXI-1120. Pressure, concentration and pH voltages were all connected to the SCXI-1300. The LabVIEW Virtual Instrument circuit diagrams are shown in Appendix B.

All of the temperature sensors be connected to data acquisition and will not need to be manually logged. Manual intervention should only be required to turn on and off the power to the heater tube once the system has been brought to operating conditions. The data acquisition system will log the temperature sensors every minute. A CJC thermocouple will be used to subtract out the error produced from the wire connection points. CJC's are very accurate thermocouple that produces a voltage from room temperature. This voltage is used to subtract out the voltage produced from each wire connection point.

A Cole-Parmer conductivity flow cell meter will measure the exit stream NaCl concentration with an accuracy of ± 0.3 percent. A calibration curve, developed by Rogers (1997), was verified and added into LabVIEW to provide direct concentration readings. Preferential hideout of one ion over another will not be investigated in this study. Preferential hideout is when one of the ions accumulates in the crevice more than

another. This could cause an error when calculating crevice efficiencies because ions have different conductivities. For example, if Na^+ hides out preferentially, the conductivity cell would read higher than expected during the hideout phase and lower than expected during the return phase, since the conductivity of Cl^- and resulting H^+ and OH^- ions is higher than Na^+ . The specific conductance of Na^+ , Cl^- , OH^- and H^+ is shown in Table 4.2.

Table 4.2. Specific Conductance of Interest Ions

Ion	Specific Conductance (Siemens cm^2/mol)
Na^+	50.1
Cl^-	76.3
OH^-	187
H^+	368

4.5 Crevice Packing

Packing the crevice is required to initiate the salt accumulation process in the crevice. The packing material simulates typical corrosion products that normally accumulate over time. A clean, concentric crevice will not accumulate a relevant amount of NaCl because there is no bulk flow restriction, so flushing effectively occurs.

Thornel P-75S Carbon fiber will be used for this experiment. The carbon fiber comes off the spool in a single cord made of thousands of inter-twisted strands of carbon fiber. Each strand resembles a single dark brown human hair. Twice the amount of required carbon fiber will be weighed out and separated into two cords. Each cord will be cut up into 4 cm strips and kept in two separate piles. The cords from one pile will be laid parallel to each other, with a space about the same width as the cord, until enough has been used to create a 4 cm by 4 cm mat. The same process will be repeated on top of the first mat, except that the cords will be laid perpendicular to create a crisscross mesh. This process will be repeated, slightly off setting each layer, until all of the carbon fiber in a pile is used up. Next, an exactor knife will be used to precisely cut the two quilts into 3 cm by 3 cm squares. The crevice has a radial length of 6 cm with a height of 3 cm. Strands from each quilt will then be removed until the desired combination weight is achieved. The overall objective is to form identical weight quilts with irregular porous channels, one for each half of the crevice. Once the quilts have been precisely weighed, they will be carefully squished in between the tube and support plate crevice. A void fraction porosity level of 30 percent will be used, which requires 0.6258 grams of carbon fiber, with a density of 2.0 g/cm^3 for the crevice volume in this study.

4.6 Experimental Procedure

When appropriate, pure NaCl crystals will be mixed with micro-pure de-ionized water in the feed tank. The NaCl crystals are 99.99 percent pure and will completely

dissolve in the de-ionized water. ETA and PAA will also be added to the feed solution for particular runs and will be discussed in more detail at the end of this section. A Cole-Parmer mixer will be used to mix the feed solution for 1 hour. A conductivity and pH measurement will be taken to establish a concentration baseline and verify complete mixing. Once the feed solution is prepared the entire system will be turned on and the fluid will be pumped at 20 ml/min.

The temperature in the autoclave must be gradually increased to maintain system stability. If the temperature is raised too quickly, early boiling will occur in the autoclave. Early boiling creates a steam pocket at the top of the autoclave and forces a surge of liquid out. This surge of liquid directly reduces the pressure in the system and reduces the flow rate until the pressure builds back up to the back pressure regulator setting. If boiling persists, this process will continue and stability will never be reached. It is important that the autoclave be completely filled with liquid to ensure that the crevice is sufficiently submerged when the autoclave heater tube is turned on.

The final operating condition for the system is at 525 °F and 870 psig. The bulk water temperature in the autoclave will be elevated at a rate of 50 °F per hour with the pressure set well above the saturation limit. Pressure will only be adjusted twice, first at 450 psig and finally at 870 psig, to reduce the risk of boiling in the autoclave. It will take about 12 hours to reach operating conditions and must be done manually since the temperature controllers are not under software control. Ideally, the system should be right on the edge of saturation, but not at boiling, to ensure that boiling occurs when the

heater tube is turned on. This will also guarantee that the amount of heat flux put across the crevice is utilized entirely as superheat.

The system will operate for 24 hours to verify steady state before the heater tube will be turned on. When the heater tube power is turned on, a slight surge of outlet fluid should be expected. This indicates that a very small steam pocket has been formed at the top of the autoclave. The heater tube will be turned off after the conductivity of the exit stream rises back to its original feed value. At a heater power of 150 watts with a feed solution of 50 ppm NaCl, this should take around 11 hours. Once the heater power is turned off, a momentary drop in system pressure should also be expected since the small steam pocket is now being displaced with fluid. In a short period of time, the exit stream conductivity should dramatically increase indicating solute release. After about 5 hours, all of the salt should have been returned, based on results obtained by Rogers (1997). Another run of DI can follow on the next day to verify that the system has returned to baseline and that no contamination has occurred.

Table 4.3 illustrates the runs that will be performed. The Solution Type Run Matrix shows that there is 5 different solution types that will be tested. DI water will be used to establish system baseline and will be run before each of the other solution types. This assures that the simulator has been returned to a known state and that no contamination has occurred from the previous solution type.

Table 4.3. Solution Type Run Matrix

Solution Type Run Matrix			
Order (Set 1)	Order (Set 2)	Order (Set 3)	Order (Set 4)
DI	DI	DI	DI
DI, NaCl	DI, NaCl	DI, PAA, ETA, NaCl	DI, NaCl
DI	DI	DI, PAA, ETA, NaCl	DI
DI, PAA, ETA	DI, PAA, ETA, NaCl	DI	DI, PAA, ETA, NaCl
DI	DI		DI, PAA, ETA, NaCl
DI, PAA, ETA	DI, PAA, ETA, NaCl		DI
DI	DI, PAA, ETA, NaCl		DI, NaCl
DI, NaCl	DI		DI
DI	DI, PAA, ETA		
DI, ETA	DI		
DI	DI, ETA		
	DI		
	DI, PAA, ETA		
	DI		

This assures that the simulator has been returned to a known state and that no contamination has occurred from the previous solution type. Once the crevice is packed and ready, all of the runs will be performed. Table 4.4 illustrates a typical run cycle. The table shows that it would take at least 6 days to test out only one solution type, and two additional days for each additional solution type tested. All of these runs will be completed with a constant autoclave pressure, and heat flux across the crevice.

Table 4.4. Typical Run Cycle at a Specific Porosity

Order	Activity	Duration (Days)
1	Prepare the crevice and feed solutions	2
2	Turn on the system and bring up to operating conditions	1
3	Run DI water	1
4	Run a solution type	1
5	Repeat steps 3 & 4 to run another solution type, or run DI water to cool down and shutoff the system	1
		6 Days Total

5 RESULTS AND DISCUSSION

The main objectives of this research were to study the effect of PAA addition on the mass accumulation, diffusion rate and superheat inside a simulated steam generator crevice. PAA is hoped to increase the surface tension in the crevice, and thus reduce the amount of corrosion buildup. Since PAA has such a large pH level, ETA was added to bring the pH level down. High pH levels are known to accelerate the concentration effects in steam generator crevices. Comparisons of different chemical feed stocks were performed to isolate the effects that each chemical has on the exit steam, as shown in Table 4.1. DI water was used to establish system baseline and was run between other chemicals to assure that no contamination occurred. The method of hideout and return was used to determine the amount of salt accumulation and diffusion rate inside the crevice.

As shown in Table 4.1, background variables remained constant for all experiments performed. For instance, 150 W of power was applied across the crevice for each run. This resulted in a temperature inside the heater core of about 700 °F and a temperature at the crevice wall of 525 °F for each run. Figure 5.1 shows a typical temperature profile inside the heater core and at the crevice wall for one of the runs. Since these did not vary, the rest of the runs are provided in Appendix C. The temperature profile shown in Figure 5.1 confirms that the temperature inside the heater and at the crevice wall remained constant through the entire run. It also provides a

convenient way to determine exactly when the heater tube was turned on and off for each particular run. Based on the length of tubing between the autoclave and the conductivity flow cell, it has been calculated that it should take a minimum of 19 minutes for the fluid from the autoclave to reach the conductivity flow cell. Therefore, a change in the exit NaCl concentration and pH will be delayed by about 20 minutes after the heater tube is turned on.

Figure 5.1. Temperature Profile Inside the Heater and Crevice Wall with DI+NaCl Feed (Run on 990212)

5.1 Superheat

A variety of different feed stocks were used with the same carbon fiber packed crevice, as shown in Table 4.1. For all of the different feed stocks, the steady state superheat value was about 15 ± 5 °F. Initial superheat, after the heater tube was turned on, was usually 5 to 10 °F higher, but steadied out after about 150 minutes. The superheat profile for one of the runs is shown in Figure 5.2, with the rest provided in Appendix C. Four thermocouples are plotted in Figure 5.2 A, C, F and G. These are the first, third, seventh and eighth thermocouples arranged in a helical pattern inside the heater tube.

**Figure 5.2. Crevice Superheat with DI+PAA+ETA+NaCl Feed
(Ran on 990204)**

Four sets of runs were performed. For set 1 performed in February, the superheat across the thermocouples was tight and constant for all of the runs, even for those with different feed stocks. There were only a few degrees of difference between the thermocouples and the reading remained steady for the duration of the run. From the set 1 results it appears that the steady state superheat was unchanged by the addition of ETA, PAA or NaCl. At least one run of each of the chemicals was performed in this set. For sets 2,3 and 4 performed in May, the superheat across the thermocouples was wider spread and random for all the runs, even for the DI runs alone. The random readings in data acquisition of the thermocouples was due to a damaged data acquisition card during an electrical accident. The damaged data acquisition card was not detected immediately since temperature readings were in the correct range, but drifting. For this reason, the superheat from the second set of runs was not used and repeatability of the first set of runs was not verified. Manual readings of the thermocouples were logged at heater on and off for all of the runs and helped confirm that superheat was stable throughout. Superheat for each thermocouple was calculated and is provided in Table 5.1. An average superheat for each solution type is also shown in the table. Comparing PAA-free runs against PAA runs showed very little or no change. The average superheat for DI and ETA runs with and without PAA only changed 0.3 °F. The average superheat for DI and NaCl runs with and without PAA didn't change at all.

Table 5.1. Manual Superheat Measurements at Heater On/Off

Solution Type	Superheat (F)					
	Date	A - Bulk	C - Bulk	F - Bulk	G -Bulk	Ave
DI+ETA	2/17	15.1	11.6	23.1	15.9	16.4
DI+ETA	5/18	14.2	27.2	11.0	5.6	14.5
						15.5
DI+ETA+PAA	2/4	13.1	15.0	16.6	18.6	15.9
DI+ETA+PAA	2/10	13.1	15.0	16.9	15.1	15.0
DI+ETA+PAA	5/15	16.4	27.2	11.0	5.6	15.1
DI+ETA+PAA	5/21	16.4	27.2	11.0	5.1	14.9
						15.2
DI+NaCl	1/31	15.9	18.9	16.9	20.8	18.1
DI+NaCl	2/13	13.5	12.7	16.5	19.4	15.5
DI+NaCl	6/1	14.6	27.2	14.6	11.0	16.9
DI+NaCl	6/14	11.0	27.2	14.6	11.0	16.0
DI+NaCl	6/21	12.8	27.2	12.8	11.0	16.0
						16.5
DI+NaCl+PAA+ETA	5/9	14.6	25.4	11.0	5.6	14.2
DI+NaCl+PAA+ETA (1)	5/12	20.0	32.6	18.2	11.0	20.5
DI+NaCl+PAA+ETA (2)	5/12	12.8	23.6	7.4	0.2	11.0
DI+NaCl+PAA+ETA (1)	6/10	11.0	25.4	14.6	11.0	15.5
DI+NaCl+PAA+ETA (2)	6/10	12.8	27.2	14.6	11.0	16.4
DI+NaCl+PAA+ETA (1)	6/18	14.6	29.0	14.6	11.0	17.3
DI+NaCl+PAA+ETA (2)	6/18	27.2	29.0	14.6	12.8	20.9
						16.5

5.2 DI (Baseline)

The first few runs were performed to establish a system baseline. The system baseline is a standard level of pH and NaCl concentration on a normal run of DI water. Ions from DI will be reported as an NaCl concentration for reasons mentioned in the Experimental Design section. At operating conditions with the heater tube turned off, the pH and NaCl concentration reads around 5.5 ± 0.5 pH and -2.0 ± 1 ppm, respectively. DI water runs were performed between each of the other runs to verify that no contamination occurred and that the system returned to baseline levels.

A small opposite reaction of hideout and return was observed with straight DI water. Right after the crevice heater was turned on, there was a small spike in NaCl exit concentration instead of a drop. An enlarged plot of NaCl exit concentration for DI water is shown in Figure 5.3. This figure shows a plot of NaCl exit concentration with respect to time. Notice a small spike about 20 minutes after the heater tube was turned on. Since the pH and total conductivity probes are at the exit stream of the simulator, the autoclave

**Figure 5.3. Expanded Plot of NaCl Concentration with DI Feed
(Run on 990212)**

residence time will always cause about a 20 minute delay in the readings, as previously mentioned in Section 5.0. The small spike could indicate that preferential hideout of Na^+ was occurring. After the heater was turned on, Na^+ was hiding out while Cl^- continued down stream. Cl^- turns into HCl , leaving a large number of H^+ and OH^- ions in the exit stream. Since the specific conductance of H^+ and OH^- is so much larger than Na^+ or Cl^- , shown in Table 4.2, a large spike was observed in the exit stream. The opposite effect was shown after the heater tube was turned off. When the heater tube was turned off, there was a small dip in the specific conductance. This is most likely from the slow return of Na^+ ions and the reformation of the H^+ and OH^- ions into H_2O , resulting in a measurable drop in total conductivity.

An examination of the pH versus time for this run seems to confirm the argument of preferential hideout. Figure 5.4 shows the enlarged pH profile for the same run. At

exactly the same time the NaCl concentration (total conductivity) spikes, the pH drops due to the formation of acidic HCL. And at the same time the NaCl concentration drops, after the heater is turned off, the pH peaks.

**Figure 5.4. Expanded Plot of Autoclave Exit pH with DI Feed
(Ran on 990212)**

5.3 DI and ETA

ETA was used as an additive to PAA to bring the pH level down. It is important to understand the effects that ETA has alone. This will help to us to distinguish what changes are caused from ETA and PAA alone in the future. The pH diagram for ETA remained close to the baseline, while the NaCl diagram was dramatically changed with a spike at heater on and a 40 minute drop in concentration at heater off. The ETA curve was exactly the opposite of the standard hideout and return curve.

The DI and ETA solution was prepared by adding enough ETA to bring the pH up to 9.5 ± 0.5 pH. It was found that the initial NaCl concentration was directly related to how much ETA was added into the solution. If the pH of the water was low (5 pH), more ETA had to be added which yielded a much higher initial NaCl concentration. For a high pH water (6 pH), less ETA was required and produced a lower initial NaCl concentration. The variation of the initial NaCl concentration varied widely between 36 ppm and 70 ppm depending on how much ETA was added.

Two tests were performed using a DI and ETA feed stock. The DI and ETA tests compared very closely with the DI baseline runs by showing a small drops and peaks in the pH levels when the heater power was applied and removed. A typical pH plot for one of the DI and ETA runs is shown in Figure 5.5, the rest of the plots are provided in Appendix C. After the heater power was applied there was a small drop in pH, about 0.25 pH. After the heater power was turned off, there was a small peak in the exit pH, again about 0.25 pH. During the 250 minutes that the heater power was applied, there

**Figure 5.5. Autoclave Exit pH with DI+ETA Feed
(Ran on 990518)**

was a small sinusoidal fluctuation in the exit pH that did not show up in any of the DI baseline runs. The pH plot for DI and ETA relates very closely with DI alone except for the sinusoidal fluctuation shown in Figure 5.5. The sinusoidal fluctuations also showed up in the PAA and NaCl runs where ETA was added.

DI and ETA had a much larger effect on the NaCl concentration than DI alone. A typical NaCl concentration graph for DI and ETA is shown in Figure 5.6, additional graphs are supplied in Appendix C. When the heater was turned on, there was a 6 ppm spike of NaCl concentration at the exit stream. This spike of NaCl lasted for 20 minutes

and was followed by a 40 minute 1 ppm drop in NaCl concentration when the heater tube was turned off.

The DI and ETA curve is exactly the opposite of the standard hideout and return curve. The DI and ETA spikes at heater on and drops at heater off. Since ETA will always be added with PAA, this opposite reaction might make the normal hideout and return appear to have less when PAA and ETA is added. The anomaly will be investigated in more detail in section 5.6.

**Figure 5.6. NaCl Exit Concentration with DI+ETA Feed
(Ran on 990518)**

5.4 DI, ETA and PAA

A DI, ETA and PAA feed without NaCl was investigated to determine how it changed the exit NaCl concentration and pH from baseline conditions. DI, ETA and PAA compared closest with the DI and ETA runs. The addition of PAA did not appear to change the pH curve from DI baseline conditions. The effects of ETA appeared to dominate the NaCl exit concentration diagram for these runs as well.

PAA is a very basic solution, with a pH of 11. Since high pH levels are known to accelerate the corrosion effects, ETA was used to bring the pH down to a reasonable level. ETA was added while the solution was mixing to bring the pH down to 9.5 ± 0.5 pH. As with DI and ETA solutions, the amount of ETA added to bring the pH down controlled the initial NaCl concentration.

Four tests with DI, ETA and PAA were performed. All four tests were very similar in nature to the DI and ETA runs previously discussed. As previously mentioned, the solution was introduced to the system at 20 ml/min and 150 W of power was applied across the crevice. Figure 5.7 shows one of the DI, ETA and PAA pH response plots to heater on/off; additional figures are provided in Appendix C. For this run the heater power was applied for 750 minutes. Similar to DI water alone and DI with ETA, there was a 0.25 pH change when the heater tube was turned on and off. The addition of PAA or ETA did not seem to impact the pH data.

**Figure 5.7. Autoclave Exit pH with DI+PAA+ETA Feed
(Ran on 990521)**

The effects of ETA appeared to dominate the NaCl exit concentration diagram for the DI, ETA and PAA feed. The NaCl concentration curve for DI, ETA and PAA was the same as the curve produced by the DI and ETA solution, and is shown in Figure 5.8. ETA was responsible for the 20 minute, 6 ppm spike of NaCl concentration when the heater tube was turned on and a 40 minute, 1 ppm NaCl concentration drop when the heater tube was turned off. These are the same characteristics that were seen for the DI and ETA feed stream shown in Figure 5.6. The sinusoidal nature of the curve during the time the heater is on is also the same.

The accumulation data for the hideout and return of DI, ETA and PAA is shown in Table 5.2. Table 5.2 shows that two runs were done in set 1 and two runs were done in set 2. The hideout accumulation mass for the first and second runs performed in set 1 were, 1.46 and 1.58 mg, respectively. The average accumulation for sets 1 and 2 were, 1.52 and 0.74 mg, respectively. The overall average hideout accumulation for all of the runs of DI, ETA and PAA were 1.13 mg.

It was expected that the same number of ions that hideout should equal the number of ions in the return phase. In that case the accumulation and return calculations should be equal. A couple of the runs compared closely with each other, with accumulations differences varying from 2 % to 12 %. The first DI, ETA and PAA runs had a significantly larger return value than the rest. One interesting thing about this run was that two prior runs were considered bad for odd levels of NaCl and pH. One run of DI, ETA, PAA and NaCl and one run of DI were run prior to this run. The first run had an extremely high level of NaCl concentration and the second DI run appeared to have massive amounts of ETA in the concentration curve, similar to Figure 5.8. This could indicate that some of the ETA was trapped inside that crevice and release during the return of this run. That would describe why the return was significantly larger than the number of ions accumulated during the hideout phase.

Solution Type	Date	Set	Initial NaCl (ppm)	Hideout (mg)			Return (mg)			Diff (cm ² /sec)		
				Real	Ave	Adj	Real	Ave	Adj	Real	Ave	Adj
DI+ETA	02/17	1	2.7	0.24	-	-	0.20	-	-	-	-	-
DI+ETA	05/18	2	37.0	1.50	-	-	0.50	-	-	-	-	-
						0.67			0.36			
DI+ETA+PAA	02/04	1	19.1	1.46	-	1.07	3.90	-	2.78	-	-	-
DI+ETA+PAA	02/10	1	13.0	1.58	1.52	1.19	1.62	2.76	0.50	-	-	-
DI+ETA+PAA	05/15	2	60.5	0.76	-	1.15	0.67	-	1.79	-	-	-
DI+ETA+PAA	05/21	2	30.9	0.71	0.74	1.10	0.38	0.53	1.50	-	-	-
						1.13			1.64			
DI+NaCl	01/31	1	42.3	6.41	-	8.08	6.19	-	9.38	4.69	-	7.77
DI+NaCl	02/13	1	38.2	8.20	7.31	9.65	7.20	6.69	10.39	4.80	4.75	7.87
DI+NaCl	06/01	2	41.6	9.59	9.59	8.96	11.93	11.93	9.88	10.25	10.25	7.82
DI+NaCl	06/14	4	41.6	9.53	-	8.52	10.48	-	9.34	8.64	-	7.89
DI+NaCl	06/21	4	42.7	10.40	9.96	9.39	11.58	11.03	10.43	8.29	8.46	7.84
						8.96			9.88			7.82
DI+NaCl+PAA+ETA	05/09	2	49.4	11.18	-	10.51	8.48	-	9.13	7.75	-	5.61
DI+NaCl+PAA+ETA (1)	05/12	2	50.8	8.66	-	7.99	7.33	-	7.98	7.95	-	5.81
DI+NaCl+PAA+ETA (2)	05/12	2	50.8	11.71	10.52	11.03	13.15	9.65	13.80	10.04	8.58	7.90
DI+NaCl+PAA+ETA (1)	06/10	3	58.4	8.12	-	9.63	11.34	-	10.82	5.9183	-	6.36
DI+NaCl+PAA+ETA (2)	06/10	3	58.4	8.74	8.43	10.15	10.31	10.82	9.79	6.0754	6.00	6.82
DI+NaCl+PAA+ETA (1)	06/18	4	74.3	10.35	-	9.61	10.75	-	10.62	4.9279	-	6.82
DI+NaCl+PAA+ETA (2)	06/18	4	74.3	10.82	10.59	10.06	10.13	10.44	9.99	4.5691	4.75	6.28
						9.94			10.30			6.44

Table 5.2. Real and Adjusted Mass Accumulation and Diffusion Rates for Hideout and Return

**Figure 5.8. NaCl Exit Concentration with DI+PAA+ETA Feed
(Ran on 990521)**

5.5 DI and NaCl

The results obtained in this study compared closely with results from previous researchers (Mann and Castle, 1983; Balakrishnan, 1991; Rogers, 1997). NaCl did accumulate in the crevice with an applied heat source and a sufficiently fouled packed crevice. When the heat flux was applied, there was an immediate concentrating effect across the crevice and when the heat flux was removed, there was an immediate return of impurities through diffusion taking residence time into account.

DI and NaCl were prepared by mixing 2.500 grams of NaCl and 50 liters of DI water. After the feed solution was well mixed, usually around an hour, it resulted in a concentration of around 38 ± 2 ppm with a pH of 5.5 ± 0.5 pH. The 38.2 ppm concentration was consistently lower than the target 50 ppm due to the practice of manually filling the tanks to the 50 liter mark. Subsequent testing showed that the tank marks were on the high side. Since the tank's markings were used during the runs, the extra volume of DI water caused the drop in initial NaCl concentration. The correct weight of NaCl for a target weight of 50 ppm was verified. Five runs of NaCl were performed which all compared very closely with each other, verifying the NaCl makeup method was consistent. The initial pH, shown in Figure 5.9, compared very closely with a standard DI run. The addition of NaCl had essentially no effect on the initial pH level of standard DI water. NaCl did effect the pH when the heater was applied. Figure 5.9 shows that there was a 70 minute, 0.5 pH drop when the heater tube was turned on and a 200 minute, 0.7 pH peak when the heater tube was turned off. When the heater tube is

turned on, Na^+ and Cl^- ions hideout in the crevice and are released when the heater tube is turned off.

A typical hideout and return graph is shown in Figure 5.10. The additional hideout and return graphs are shown in Appendix C. The hideout phase lasted for 210 minutes and when the heater power was eliminated there was a significant return of sodium chloride, which lasted for 160 minutes.

**Figure 5.9. Autoclave Exit pH with DI+NaCl Feed
(Ran on 990213)**

The hideout and return accumulation weights for NaCl were calculated and shown in Table 5.2. The NaCl hideout and return accumulation weights from Table 5.2 were

used to calculate the differential error for each of the runs, shown in Table 5.3. The errors ranged from as low as 3% to 20%. In previous studies by Rogers (1997) and

Table 5.3. Error Between Hideout and Return Accumulation For Each Run

Solution Type	Date	Set	Hideout	Return	Error
DI+NaCl	01/31	1	6.41	6.19	3%
DI+NaCl	02/13	1	8.20	7.20	12%
DI+NaCl	06/01	2	9.59	11.93	20%

Balakrishnan (1991), errors ranging between 30 and 50% were not uncommon. This shows that the simulator performed quite well when compared with other experiments. The simulator did perform quite poorly on repeatability between sets of runs. Looking in more detail at Table 5.2, it shows that the hideout changed from run to run. For example, it changed from 6.41 to 8.20 and then finally to 9.59 for the third run. This shows that some additional background variable might be responsible for this large difference, and will be discussed in more detail in section 5.7

**Figure 5.10. NaCl Exit Concentration with DI+NaCl Feed
(Ran on 990213)**

5.6 DI, ETA, PAA and NaCl

It was expected that PAA would reduce the amount of NaCl that accumulates in the crevice. With the addition of PAA, the pH and NaCl curves were both effected. It was expected that the DI, ETA, PAA and NaCl curves would resemble the DI and NaCl curves. Unexpectedly, the DI, ETA, PAA and NaCl pH curve appeared more like the baseline DI curve. PAA seemed to transform or remove the NaCl effects out of the pH curve. PAA did reduce the amount of NaCl accumulation in the simulated steam generator crevice. The effective diffusion was also lowered by PAA when examining runs within the same set, possibly from an increase in the capillary pressure.

A solution of DI, ETA, PAA and NaCl was prepared by mixing 2.500 grams of NaCl, 4.5977 grams of PAA, and enough ETA to standardize the pH level to 9.8 ± 0.5 pH. Four runs were performed; two of which were back to back. A plot of pH for DI, ETA, PAA and NaCl is shown in Figure 5.11; additional figures are provided in Appendix C. The pH data for DI, ETA, PAA and NaCl was almost exactly the same as the baseline runs of DI water shown in Appendix C.

A typical hideout and return graph for this mixture is shown in Figure 5.12. The additional hideout and return graphs are shown in Appendix C. For the DI, PAA, ETA and NaCl run the return phase only lasted for 136 minutes, compared with 174 minutes

**Figure 5.11. Autoclave Exit pH with DI+PAA+ETA+NaCl Feed
(Ran on 990618)**

with DI and NaCl alone. This also indicates that less mass accumulation occurs. Both the DI, NaCl and DI, ETA, PAA, NaCl plots have the same 9 ppm peak change in concentration when the heater tube was turned off.

It was expected that the equilibrium weight of NaCl would decrease by adding PAA. PAA should increase the surface tension in the crevice. Increased surface tension increases the capillary pressure in the crevice and results in a reduced amount of NaCl in the return. The equilibrium weight of NaCl did appear to decrease when PAA was added to the feed stream only when comparing runs in the same set. Table 5.2 shows a summary of the main differences between the NaCl mass accumulation and effective

**Figure 5.12. NaCl Exit Concentration with DI+PAA+ETA+NaCl Feed
(Run on 990512)**

diffusion rates for PAA and PAA-free feed streams. When comparing runs done in the same set, the mass accumulation of NaCl in the crevice for a DI and NaCl feed was 11.93 mg. This was quite large when comparing to a DI, ETA, PAA and NaCl run done in the same set, with only 8.48 and 7.33 mg mass accumulation.

Since PAA increases the surface tension, it should also decrease the effective diffusion, or rate at which ions diffuse out of the crevice during the return phase. The effective diffusion rate for DI and NaCl was $10.25 \text{ cm}^2/\text{sec}$ compared with 7.75 and $7.95 \text{ cm}^2/\text{sec}$ for DI, ETA, PAA and NaCl feed. PAA did appear to reduce the amount of NaCl accumulation and lowered the effective diffusion rate inside the crevice when

comparing only one or two runs in the same set. Since only one set of runs had both DI and NaCl and DI, ETA, PAA, and NaCl performed together, the statistical significance of this conclusion will be investigated in more detail in section 5.7.

One concern was that the opposite reaction caused from ETA would make the DI, ETA, PAA and NaCl run appear to have less hideout and return. The DI and ETA would spike at heater on and drop at heater off. Since this was exactly the opposite of the DI and NaCl curve, the addition of ETA and PAA might cause the integration of the curve to be less. Table 5.2 shows that the magnitude of the DI and ETA was insignificant when compared with the difference of DI and NaCl with DI, ETA, PAA, and NaCl since it was actually larger. The accumulation weights for hideout and return were larger with PAA solutions compared to PAA-free solutions. PAA clearly did not appear to reduce the amount of NaCl accumulation in the crevice and ETA had no counter effect.

A back-to-back run of DI, ETA, PAA and NaCl was performed to verify that no contamination from accumulation occurred over time. As shown in Figure 5.13, the hideout and return curves are almost identical. The first curve returned 11.34 mg of NaCl and the second curve returned 10.31 mg. This is a difference of only 1 mg which is within the standard error limits of the DI, ETA, PAA and NaCl runs. So no contamination or accumulation of PAA was experienced.

**Figure 5.13. NaCl Exit Concentration with Back-to-Back
DI+PAA+ETA+NaCl Feed (Ran on 990610)**

5.7 Error and Repeatability

A large number of errors were present when comparing runs across different sets. Each set of simulator runs were quite different from the previous and was responsible for most of the error in the results. A statistical technique known as blocking was used to adjusted out the effects of different simulator run sets. From a statistical perspective, the addition of PAA had no effect on the hideout, return and diffusion rate of NaCl in the crevice.

A run chart was generated to determine if there were any trends, shifts or cycles in the data. Figure 5.14 shows the run chart of raw accumulation data for hideout, return and diffusion rates out of the crevice. The chart shows that there is a large shift in data, based on the different sets of runs performed. Three main sets of runs were performed. Most of the sets had a variety of different feed stocks types used, which should result in two main groups of data: one group of high values and one group of low values. Since the hideout and return accumulation of type 1 (DI and ETA) and type 2 (DI, ETA and PAA) feed stocks were quite small, they should result in points in the 0-2 mg range. For the accumulation of type 3 (DI and NaCl) and type 4 (DI, ETA, PAA and NaCl) feed stocks the accumulation should result in the 8-12 mg. Clearly this is not the observation for the raw accumulation and diffusion data shown in Figure 5.14.

Figure 5.14. Run Chart for Hideout, Return and Diffusion Rate

For the first set or runs that were performed in February, there is no distinction between the high and low sets. Also, a large amount of variation can be seen within the high accumulation weights calculated in May and June. Upper and lower variation as high as 8 mg is common for the high accumulation weights. This chart shows that the set of runs has a significant impact on the accumulation and diffusion rates.

A standard statistical practice is to adjust out the background variable, also known as blocking. Blocking subtracts out the average value within a set and add back in the average value of the response variable for the factor under study. The integrity of the difference between each runs is unchanged and the overall average for the entire group is

Figure 5.15. Adjusted Run Chart for Hideout, Return and Diffusion Rates

unchanged under blocking. Blocking just shifts the set of data to an average value for the entire series of that feed stock type. Table 5.2 shows the adjusted and average values for each of the response variables under study. Figure 5.15 shows the run chart of adjusted accumulation and diffusion rates out of the crevice.

With the adjusted values shown in Figure 5.15, there is a clear difference between the high and low mass accumulation calculations for the first set of runs performed in February. Also, the spread of values for the high accumulation calculations performed in May and June were much tighter. The variation is only around 2 mg for the high accumulation calculations in May and June. Overall, there is a much more even spread of points which represents a standard distribution of points.

At least two runs were performed for each set of feed stock combinations. Differentials and percent errors were calculated between different runs in the same set and between different sets for the same feed stock type, shown in Table 5.4. For example, the percent error of hideout mass accumulation for DI, ETA and PAA between two runs in the same set were 8% and 7%, 8% error between two runs in set 1 and 7% error between two runs in set 2. The error between all of the runs performed for DI, ETA, and PAA was 52%. When adjusting out the difference between the sets, the error changes to only 10% with a delta of ± 0.12 . This means that the hideout mass accumulation calculated in Table 5.2 could be 1.13 ± 0.12 mg, or 1.01 to 1.25 mg respectively. These calculations show that the difference between sets had a significant impact on the error of the data.

The large difference between sets appeared to be caused from the addition of ETA. As was mentioned before, ETA had a significant impact on the exit NaCl concentration curve. More ETA resulted in a higher initial concentration, and hideout and return values. With DI, ETA, PAA and NaCl only a small amount of ETA (usually a couple of milliliters) had to be added to bring the pH up to 9.8, whereas with DI and ETA, a large amount of ETA had to be added (usually around 20-30 milliliters). This information is confirmed in the table since the error between sets goes down as less ETA is added to the feed stream. Comparing overall percent error between solution types shows that the error goes down for both hideout and return moving down the table. For example, the overall percent error moves from 84% down to 26% for hideout.

Solution Type	Hideout				Return				Diffusion Rate				
	Set	Real		Adj	Diff	Real		Adj	Diff	Real		Adj	
		Set %	All %	All %		Set %	All %	All %		Set %	All %	All %	
DI+ETA	1	1.26		84%	-	0.30		60%	-	-	-	-	
					0.73				0.21			-	
DI+ETA+PAA	1	0.12		52%	10%	2.28		81%	82%	-	-	-	
DI+ETA+PAA	2	0.05		-	-	0.29		-	-	-	-	-	
					0.12				1.34			-	
DI+NaCl	1	1.79		27%	20%	1.00		39%	16%	0.10		54%	1%
DI+NaCl	4	0.87		-	-	1.09		-	-	5.45		-	-
					1.65				1.45				0.10
DI+NaCl+PAA+ETA	2	0.53		26%	6%	1.16		27%	17%	0.20		40%	11%
DI+NaCl+PAA+ETA	3	0.62		-	-	1.03		-	-	0.16		-	-
DI+NaCl+PAA+ETA	4	0.47		-	-	0.62		-	-	1.15		-	-
					0.62				1.62				0.75
Total % Error Between DI+NaCl and DI+NaCl+PAA+ETA													
													2.27
													3.06
													0.85

Table 5.4. Real and Adjusted Error for Hideout and Return Accumulation and Diffusion Rates

The unadjusted percent errors between DI and NaCl runs of the same set for hideout and return were 22% and 8%, respectively. 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 differences between sets, the percent error was only 20%. This might indicate that other studies had a problem with error between sets as well.

Statistics shows that there is no difference between the hideout and return of DI and NaCl with DI, ETA, PAA and NaCl. Subtracting out the average hideout and return values between DI and NaCl with DI, ETA, PAA and NaCl gives 0.89 and 0.42, respectively. These numbers are much smaller than the error bars for the combination of DI and NaCl with DI, ETA, PAA and NaCl deltas. For example, the combined error bar for hideout alone would be 2.27 mg ($1.65 + 0.62$ mg). This means that the difference between DI and NaCl with DI, ETA, PAA and NaCl must be larger than 2.27 mg to be significant. Since the errors for both hideout and return were much larger than the differences, PAA had no effect on the accumulation rates of NaCl.

Diffusion rate calculations were much more stable over all the runs when compared against hideout and return values. All of the real diffusion rate errors were in the low single digit percent range, whereas the real percent errors for hideout and return were usually in the two digit range. For example, the real diffusion rate error for the DI and NaCl runs were as low as 2 % compared against 22% and 14% for hideout and return, respectively. This shows that diffusion rate is a much better measure when comparing multiple runs. PAA did appear to have a small impact on the effective

coefficient. The average effective diffusion coefficient was lowered by $1.38 \text{ cm}^2/\text{sec}$, which was outside the calculated range of error $0.85 \text{ cm}^2/\text{sec}$.

6 CONCLUSION

A steam generator simulator, constructed by Rockwell International, was used to study to effects that PAA had on the corrosion process inside a crevice. The steam generator simulator simulates a single crevice formed in between the tube and tube-support plates found in a real steam generator. This experiment used a variety of feed streams, shown in Table 4.1, to determine the effect that PAA had on the salt accumulation inside the crevice. This experiment showed that when the crevice is packed with carbon fiber and a heat flux is applied there is an immediate accumulation of ions in the crevice. When the heat flux is removed there is an immediate return of the accumulated impurities through diffusion.

The addition of PAA had no effect on the mass accumulation of PAA inside the crevice. When considering error, the average hideout and return mass accumulations values were identical. The addition of PAA did lower the average effective diffusion coefficient by $1.38 \text{ cm}^2/\text{sec}$, which was outside the calculated error of $0.85 \text{ cm}^2/\text{sec}$. Through visual observation and temperature measurements at the crevice wall, PAA did not decrease the amount of system superheat and steam blanketing was not present throughout all the runs.

Each set of simulator runs was quite different from the previous. A statistical technique known as blocking was used to adjust out the effects of different simulator run sets. Using statistics, a normal distribution of points was established which greatly

reduced the error between runs. Since previous studies resulted in multiple errors, statistical techniques are highly recommended in future studies.

7 FUTURE WORK

- Effect of baked PAA on the mass accumulation of sodium chloride in the crevice.
- Effect of higher concentrations of PAA.
- Effect that different packing porosity's have on the mass accumulation and effective diffusion coefficient for sodium chloride in the crevice.

NOMENCLATURE

A	=	Heated Area (cm ²)
b	=	½ the capsule slug thickness (cm)
S	=	Surface area available for diffusion (cm ²)
C_{avg}	=	Average pore concentration (mol/cm ³)
C	=	Local concentration (mol/cm ³)
C_c	=	Capsule concentration (mol/cm ³)
C_f	=	Feed Concentration (mol/cm ³)
D_e	=	Effective diffusion coefficient (cm ² /sec)
D_o	=	Bulk diffusion coefficient (cm ² /sec)
h	=	Heat transfer coefficient (W/cm ² ·K)
J	=	Diffusion Flux (g/cm ² ·sec)
k	=	rate constant (1/sec)
l	=	Diffusion path length, or half the depth of the crevice (cm)
Q	=	Capsule feed rate (cm ³ /sec)
q''	=	Heat flux (W/cm ²)
t	=	Time (sec)
T_{sat}	=	Saturation Temperature (°F)
V_c	=	Capsule Volume (cm ³)
ρ	=	Density (g/cm ³)
ε	=	Porosity

REFERENCES

1. Adamson A.W.; Gast A.P., Physical Chemistry of Surfaces, Sixth Edition, John Wiley & Sons: New York, 1997.
2. Balakrishnan P., *Hideout and Return of Complex Mixtures in Crevices*, EPRI S407-13, Electrical Power Research Institute: Palo Alto, California, September 1991.
3. Baum A. J.; Smith-Magowen D.; Lee A. Y., *Crevice Hideout Return Testing*, EPRI NP-4678, Electrical Power Research Institute: Palo Alto, California, July 1986.
4. Brunet J.P.; Campan J.L., *Hideout of Sodium Salts in Tubesheet Crevices*, EPRI NP-5265, Electrical Power Research Institute: Palo Alto, California, July 1987.
5. Campan J. L.; Shoemaker C. E., *Sodium Hideout Studies In Steam Generator Crevices*, Presented at the Environmental Degradation in Nuclear Power Systems Conference, Traverse, Michigan, 1988.
6. Cleary J.G.; Von Nieda G.E.; Lindsay W.T., *Diffusion and Hideout in Crevices*, EPRI NP-2979, Electrical Power Research Institute: Palo Alto, California, March 1983.

7. Cohen P., *Chemical Thermohydraulics Of Steam Generating Systems*, Process Conference, Presented at the Water Chemistry and Corrosion in the Steam-water Loops of Nuclear Power Stations Conference, Sellac, France, March 1980
8. Douglas, J., *Solutions for Steam Generators*, EPRI Journal, May/June 1995, pg. 29-34.
9. Green S. J., *Solving Chemical and Mechanical Problems of PWR Steam Generators*, CEP Newsletter, July 1987.
10. Green S. J., SGOG Steam Generator Reference Book, First Edition, John Wiley & Sons: New York, 1995.
11. Lindsay W.T., *Estimation of Diffusion Coefficients for Electrolytes in Water to 300 °C*, Power Industry Research, July 1981.
12. Lumsden J.B.; Pollock G.A.; Stocker P.J., *Heated Crevice Investigation of the Effects of Feedwater Chemistry on Crevice Chemistry and Crevice Potential*, EPRI RPS520-08, Electrical Power Research Institute: Palo Alto, California, Jan 1998.
13. Lumsden J.B.; Pollock G.A.; Stocker P.J., *Hideout in Prototypic Tube/Tube Support Plate Heated Crevices*, EPRI RPS407-13, Electrical Power Research Institute: Palo Alto, California, July 1997.

14. Lumsden J.B.; Pollock G.A.; Stocker P.J., *Hideout of Na in a Prototypic SG Tube/Tube Support Plate Crevice*, EPRI RPS520-08, Electrical Power Research Institute: Palo Alto, Ca, July 1998.
15. Mann G.M.W.; Castle R., *Hideout and Return of Chloride Salts in Heated Crevices Prototypic of Support Plates in Steam Generators*, EPRI NP-5015, Electrical Power Research Institute: Palo Alto, Ca, January 1987.
16. Mann G.M.W.; Castle R., *Salt Concentration in Heated Crevices and Simulated Scale*, Electrical Power Research Institute: Palo Alto, Ca, EPRI NP-3050, October 1983.
17. Millett P.J., *Fundamental Study of Support Plate Crevice Transport Processes in PWR Steam Generators*, Master's Thesis University of Connecticut, 1989.
18. Millett P. J.; Fenton J., *Review of PWR Steam Generator Crevice Impurity Concentration Mechanisms*, Proceedings of a Conference on Steam Generators and Heat Exchangers, 1990.
19. Millett P.J., *Steam Generator Degradation: Current Mitigation Strategies for Controlling Corrosion*, CNRA/CSNI workshop, 1995
20. Munson B.R.; Young D.F.; Okiishi T.H., Fundamentals of Fluid Mechanics, John Wiley & Sons: New York, 1990.

21. Pedersen E. S., Nuclear Power, Volume 1, Ann Arbor Science Publishing: Ann Arbor, Michigan, 1978.
22. Peters, E., Introduction to Chemical Principles, Fifth Edition, Saunders College Publishing: Philadelphia, 1990.
23. Rogers P.M., *Sodium Chloride Hideout in a Simulated Steam Generator Tube and Tube Support Plate Crevice*, Master's Thesis San Jose State University, 1997.

APPENDIX A: CHEMICALS AND EQUIPMENT

1.1 Chemicals

- N₂ Gas
- Eutectic Salt Mixture (Weight Percent: 54.3% KNO₃, 45.7% NaNO₃)
- Conductivity Standard NaCl
- Culligan De-ionized Water (micro-pure)
- Sodium Chloride 99.99%
- PAA
- Monoethanol Amine (ETA)
- Inert Carbon Fibers

1.2 Equipment

- Nalgene Tanks (Cole-Parmer: 1-25 Gal, 2-50 Gal, 1-100 Gal)
- Quick Disconnects (Sunnyvale Valve: SS-QC8-D-8HC, SS-QC8-B-8PM)
- Plastic ¼" Feed Tubing
- Metering Pump (Pulsa-Feeder: 30 ml/min, 1000 psig)
- Poly Ether Ether Ketone Tubing (Length=50 ft, ID=0.25mm, OD=1.6mm)
- HP 5790 Gas Chromatograph Oven
- 1-Liter High Pressure Alloy 718 Autoclave
- 8 K Type Thermocouples (Omega)
- Electronic Pressure Sensor (Cole-Parmer)
- Water Flow Meter (Alicat: L12-30CCM-0-0)
- Pressure Gauges (PSItronics)

- pH Cell and Meter (Corning)
- Total Specific Conductance Cell and Meter (Cole-Parmer)
- Na Ion Specific Cell and Meter (Cole-Parmer)
- Cl Ion Specific Cell and Meter (Cole-Parmer)
- Backpressure Regulator
- 1 Pressure Relief Valve
- On Off Valves (Sunnyvale Valve: SS-42S4)
- Switching Valves (Sunnyvale Valve: SS-42XS4)
- 1 Check Valve (Sunnyvale Valve)
- ¼" 316 Stainless Steel Tubing
- Pentium 133 MHz Data Acquisition System
- Temperature Controllers
- Tube Fittings, Elbows, T's
- Mixer and Motor
- Low Flow Rotor Meter (40 ml/min max)
- Heater Bands (Omega)
- 1 Trash Can Heat Exchanger
- HP DC Power Supply
- Autoclave and Tubing Insulation
- Plexi-glass (20 ft)
- Crevice Assemble
- Pressure Fittings

APPENDIX B: LABVIEW VIRTUAL INSTRUMENTS

- ***Master Control VI***
- ***Input VI***
- ***Process VI***
- ***Archive VI***
- ***Display VI***

Master.vi

Last modified on 4/11/99 at 11:44 AM
Printed on 8/26/99 at 2:44 PM

Master.vi

Last modified on 4/11/99 at 11:44 AM
Printed on 8/26/99 at 2:44 PM

Input.vi

Last modified on 5/4/99 at 7:21 AM
Printed on 8/26/99 at 2:55 PM

Last modified on 5/4/99 at 7:21 AM

Printed on 8/26/99 at 2:55 PM

Process.vi

Last modified on 5/11/99 at 12:23 AM

Printed on 8/26/99 at 3:10 PM

Process.vi

Last modified on 5/11/99 at 12:23 AM

Printed on 8/26/99 at 3:10 PM

Process.vi

Last modified on 5/11/99 at 12:23 AM

Printed on 8/26/99 at 3:10 PM

Last modified on 5/11/99 at 12:23 AM

Printed on 8/26/99 at 3:10 PM

Last modified on 5/16/99 at 9:51 PM
Printed on 8/26/99 at 3:20 PM

Archive.vi

Last modified on 5/16/99 at 9:51 PM

Printed on 8/26/99 at 3:20 PM

Display.vi

Last modified on 5/11/99 at 12:58 AM
Printed on 8/26/99 at 3:34 PM

APPENDIX C: GRAPHICAL REPRESENTATION OF DATA

- ***Temperature Profiles***
- ***Superheat Diagrams***
- ***pH Diagrams***
- ***NaCl Concentration Diagrams***

Temperature Profile Inside the Heater and Crevice Wall with DI+NaCl Feed
(Ran on 990131)

**Autoclave Exit pH with DI+NaCl Feed
(Ran on 990131)**

**NaCl Exit Concentration with DI+NaCl Feed
(Run on 990131)**

Crevice Superheat with DI+NaCl Feed
(Ran on 990131)

**Temperature Profile Inside the Heater and at the Crevice Wall with DI+PAA+ETA Feed
(Ran on 990204)**

**Autoclave Exit pH with DI+PAA+ETA Feed
(Ran on 990204)**

**NaCl Exit Concentration with DI+PAA+ETA
(Ran on 990204)**

**Crevice Superheat with DI+PAA+ETA Feed
(Ran on 990204)**

Temperature Profile Inside the Heater and at the Crevice Wall with DI Feed
(Ran on 990206)

Autoclave Exit pH with DI Feed
(Ran on 990206)

**NaCl Exit Concentration with DI Feed
(Ran on 990206)**

Crevice Superheat with DI Feed
(Ran on 990206)

Temperature Profile Inside the Heater and at the Crevice Wall with Di+ETA+PAA Feed
(Ran on 990210)

**Autoclave Exit pH with DI+PAA+ETA Feed
(Ran on 990210)**

**NaCl Exit Concentration with DI+PAA+ETA Feed
(Ran on 990210)**

Crevice Superheat with DI+PAA+ETA Feed
(Ran on 990210)

Temperature Profile Inside the Heater and at the Crevice Wall with Di+NaCl Feed
(Ran on 990213)

Autoclave Exit pH with DI+NaCl Feed
(Ran on 990213)

**NaCl Exit Concentration with DI+NaCl Feed
(Ran on 990213)**

Crevice Superheat with DI+NaCl Feed
(Ran on 990213)

Temperature Profile Inside the Heater and at the Crevice Wall with DI Feed
(Ran on 990215)

**Autoclave Exit pH with DI Feed
(Ran on 990215)**

**NaCl Concentration with DI Feed
(Ran on 990215)**

Crevice Superheat with DI Feed
(Ran on 990215)

Temperature Profile Inside the Heater and at the Crevice Wall with Di+ETA Feed
(Ran on 990217)

**Autoclave Exit pH with DI+ETA Feed
(Ran on 990217)**

**NaCl Exit Concentration with DI+ETA Feed
(Ran on 990217)**

Crevice Superheat with DI+ETA Feed
(Ran on 990217)

Temperature Profile Inside the Heater and at the
Crevice Wall with DI+PAA+ETA+NaCl Feed
(Ran on 990509)

**Autoclave Exit pH with DI+PAA+ETA+NaCl Feed
(Ran on 990509)**

**NaCl Exit Concentration with DI+PAA+ETA+NaCl Feed
(Ran on 990509)**

**Crevice Superheat with DI+PAA+ETA+NaCl Feed
(Ran on 990509)**

Temperature Profile Inside the Heater and at the
Crevice Wall with DI+PAA+ETA Feed
(Ran on 990515)

**Autoclave Exit pH with DI+PAA+ETA Feed
(Ran on 990515)**

**NaCl Exit Concentration with DI+PAA+ETA Feed
(Ran on 990515)**

**Crevice Superheat with DI+PAA+ETA Feed
(Ran on 990515)**

Temperature Profile Inside the Heater and at the
Crevice Wall with DI+ETA Feed
(Ran on 990518)

**Autoclave Exit pH with DI+ETA Feed
(Ran on 990518)**

**NaCl Exit Concentration with DI+ETA Feed
(Ran on 990518)**

Crevice Superheat with DI+ETA Feed
(Ran on 990518)

Temperature Profile Inside the Heater and at the
Crevice Wall with DI Feed
(Ran on 990519)

**Autoclave Exit pH with DI Feed
(Ran on 990519)**

**NaCl Exit Concentration with DI Feed
(Ran on 990519)**

**Crevice Superheat with DI Feed
(Ran on 990519)**

**Temperature Profile Inside the Heater and at the
Crevice Wall with DI+PAA+ETA Feed
(Ran on 990521)**

**Autoclave Exit pH with DI+PAA+ETA Feed
(Ran on 990521)**

**NaCl Exit Concentration with DI+PAA+ETA Feed
(Ran on 990521)**

**Crevice Superheat with DI+PAA+ETA Feed
(Ran on 990521)**

**Temperature Profile Inside the Heater and at the
Crevice Wall with DI+NaCl Feed
(Ran on 990601)**

**Autoclave Exit pH with DI+NaCl Feed
(Run on 990601)**

**NaCl Exit Concentration with DI+NaCl Feed
(Ran on 990601)**

**Crevice Superheat with DI+NaCl Feed
(Ran on 990601)**

**Temperature Profile Inside the Heater and at the
Crevice Wall with DI+PAA+ETA+NaCl Feed
(Ran on 980610)**

**NaCl Exit Concentration with DI+PAA+ETA+NaCl Feed
(Ran on 990610)**

Temperature Profile Inside the Heater and at the
Crevice Wall with DI+NaCl Feed
(Ran on 990814)

**Autoclave Exit pH with DI+NaCl Feed
(Ran on 990614)**

**NaCl Exit Concentration with DI+NaCl Feed
(Ran on 990614)**

Crevice Superheat with DI+NaCl Feed
(Ran on 990614)

Temperature Profile Inside the Heater and at the
Crevice Wall with DI+ETA+PAA+NaCl Feed
(Ran on 990818)

**Autoclave Exit pH with DI+PAA+ETA+NaCl Feed
(Ran on 990618)**

**NaCl Exit Concentration with DI+PAA+ETA+NaCl Feed
(Ran on 980618)**

Crevice Superheat with DI+ETA+PAA+NaCl Feed
(Ran on 990618)

Temperature Profile Inside the Heater and at the
Crevice Wall with DI+NaCl Feed
(Ran on 990621)

**Autoclave Exit pH with DI+NaCl Feed
(Ran on 990621)**

**NaCl Exit Concentration with DI+NaCl Feed
(Run on 990621)**

Crevice Superheat with DI+NaCl Feed
(Ran on 990621)

APPENDIX D: SAMPLE CALCULATIONS

- ***Trapezoidal Integration of the Hideout Data***
- ***Trapezoidal Integration of the Return Data***
- ***Diffusion rate calculations***

DI+NaCl+ETA+PAA Second Hideout (990610)

```
Xraw := 1
Ybase-raw := 57.8
Yraw := {57.764, 57.701, 57.62, 57.512, 57.408, 57.299, 57.162, 57.047,
56.933, 56.803, 56.7, 56.549, 56.467, 56.383, 56.304, 56.256,
56.176, 56.096, 56.016, 55.925, 55.828, 55.757, 55.674, 55.598,
55.536, 55.478, 55.436, 55.387, 55.329, 55.261, 55.221, 55.175,
55.133, 55.101, 54.991, 54.857, 54.65, 54.492, 54.388, 54.462,
54.508, 54.388, 54.336, 54.252, 54.185, 54.045, 53.815, 53.625,
53.535, 53.586, 53.64, 53.776, 54.173, 54.364, 54.243, 54.075,
53.995, 53.909, 53.824, 53.751, 53.835, 53.799, 53.895, 54.075,
54.285, 54.501, 54.617, 54.589, 54.428, 54.256, 54.08, 53.904,
53.755, 53.594, 53.445, 53.418, 53.539, 53.777, 54.104, 54.288,
54.501, 54.849, 54.827, 54.606, 54.379, 54.16, 54.022, 53.907,
53.863, 53.875, 53.981, 54.146, 54.415, 54.704, 55, 55.131, 55.065,
54.887, 54.675, 54.513, 54.338, 54.195, 54.037, 53.944, 54.016,
54.253, 54.578, 54.943, 55.29, 55.461, 55.476, 55.319, 55.124,
54.893, 54.683, 54.528, 54.455, 54.479, 54.655, 54.897, 55.182,
55.517, 55.845, 56.062, 56.09, 55.968, 55.811, 55.672, 55.528,
55.435, 55.338, 55.262, 55.274, 55.342, 55.511, 55.723, 56.005,
56.297, 56.458, 56.43, 56.257, 56.047, 55.882, 55.749, 55.669,
55.583, 55.651, 55.559, 55.627, 55.754, 55.987, 56.476, 56.771,
56.856, 56.803, 56.676, 56.509, 56.385, 56.244, 56.142, 56.034,
55.973, 56.047, 56.249, 56.601, 57.017, 57.406, 57.68, 57.809}
```


ListPlot[Y_{raw}]

- Graphics -

X_{units} := min

Y_{units} := $\left(\frac{\text{mg NaCl}}{\text{L}} \right) \left(\frac{\text{L}}{1000 \text{ ml}} \right) \left(\frac{20 \text{ ml}}{\text{min}} \right)$

X_{time} := X_{raw} * X_{units}

Y_{baseline} := Y_{base-raw} * Y_{units}

Y_{mg/min} := Y_{raw} * Y_{units}

Y_{height} := Y_{mg/min} - Y_{baseline}

169

$$\text{Weight}_{\text{calculated}} = \sum_{n=1}^{169} \left(X_{\text{time}} * \frac{Y_{\text{height}}[[n]] + Y_{\text{height}}[[n+1]]}{2} \right)$$

-8.73679 mg NaCl

DI+NaCl+ETA+PAA Second Return (990610)

```

Xraw := 1
Ybase-raw := 58.5
Yraw := { 58.621, 58.882, 59.207, 59.783, 60.339, 60.812, 61.427, 62.284, 63.336,
64.24, 64.929, 65.502, 65.987, 66.362, 66.572, 66.814, 66.997, 67.141, 67.243,
67.342, 67.416, 67.449, 67.491, 67.517, 67.502, 67.432, 67.381, 67.321,
67.233, 67.125, 67.011, 66.871, 66.761, 66.624, 66.461, 66.338, 66.172,
66.008, 65.824, 65.68, 65.519, 65.353, 65.188, 65.029, 64.87, 64.697, 64.566,
64.418, 64.262, 64.108, 63.945, 63.795, 63.677, 63.553, 63.455, 63.391,
63.308, 63.21, 63.095, 62.926, 62.962, 62.927, 62.524, 62.341, 62.207, 62.03,
61.904, 61.783, 61.672, 61.569, 61.444, 61.337, 61.225, 61.126, 61.032,
60.953, 60.86, 60.788, 60.715, 60.64, 60.577, 60.513, 60.457, 60.396, 60.321,
60.278, 60.22, 60.175, 60.128, 60.055, 60.024, 59.956, 59.897, 59.863, 59.814,
59.792, 59.772, 59.745, 59.724, 59.703, 59.665, 59.628, 59.588, 59.541,
59.496, 59.449, 59.411, 59.379, 59.349, 59.308, 59.29, 59.273, 59.238, 59.23,
59.199, 59.181, 59.147, 59.131, 59.112, 59.107, 59.094, 59.077, 59.065,
59.053, 59.046, 59.043, 59.031, 59.02, 59.026, 59.009, 59.001, 58.984, 58.97,
58.965, 58.966, 58.959, 58.955, 58.951, 58.94, 58.911, 58.879, 58.876, 58.85,
58.838, 58.833, 58.823, 58.805, 58.799, 58.787, 58.768, 58.755, 58.739,
58.734, 58.911, 58.937, 58.832, 58.789, 58.733, 58.83, 58.811, 58.733, 58.705,
58.682, 58.662, 58.662, 58.658, 58.641, 58.648, 58.651, 58.646, 58.637,
58.656, 58.658, 58.674, 58.659, 58.738, 58.706, 58.757, 58.725,
58.618, 58.621, 58.733, 58.63, 58.643, 58.68, 58.587, 58.551, 58.549,
58.543, 58.547, 58.547, 58.551, 58.544, 58.541, 58.542, 58.548, 58.557}

```

ListPlot[Y_{raw}]

- Graphics -

$X_{\text{units}} := \text{min}$
 $Y_{\text{units}} := \left(\frac{\text{mg NaCl}}{L} \right) \left(\frac{L}{1000 \text{ ml}} \right) \left(\frac{20 \text{ ml}}{\text{min}} \right)$
 $X_{\text{time}} := X_{\text{raw}} * X_{\text{units}}$
 $Y_{\text{baseline}} := Y_{\text{base-raw}} * Y_{\text{units}}$
 $Y_{\text{mg/min}} := Y_{\text{raw}} * Y_{\text{units}}$
 $Y_{\text{height}} := Y_{\text{mg/min}} - Y_{\text{baseline}}$

197

$$\text{Weight Return} = \sum_{n=1}^{196} \left(X_{\text{time}} * \frac{Y_{\text{height}}[[n]] + Y_{\text{height}}[[n+1]]}{2} \right)$$

990213

10.3082 mg NaCl

DI+NaCl+ETA+PAA Second Diffusion (990610)

```
Yraw := ( 67.125, 67.011, 66.871, 66.761, 66.624, 66.461, 66.338, 66.172, 66.008,
65.824, 65.68, 65.519, 65.353, 65.188, 65.029, 64.87, 64.697, 64.566, 64.418,
64.262, 64.108, 63.945, 63.795, 63.677, 63.553, 63.455, 63.391, 63.308, 63.21,
63.095, 62.926, 62.962, 62.927, 62.524, 62.341, 62.207, 62.03, 61.904, 61.783,
61.672, 61.569, 61.444, 61.337, 61.225, 61.126, 61.032, 60.953, 60.86, 60.788)
```

```
Ylog := Log[Yraw]
Ylogplot := ListPlot[Ylog]
Yfit = Fit[Ylog, {1, x}, x]
Yfitplot := Plot[Yfit, {x, 0, 50}]
Show[Yfitplot, Ylogplot]
```

4.20759 - 0.0021207 x

- Graphics -

H_{crevice} := 0.5 * 3 cm

K_{slope} := 0.00212070058151768092 * $\frac{1}{1000} \frac{1}{\text{sec}}$

Deffective = (K_{slope}) $\left(\frac{4}{\pi}\right)$ (H_{crevice})²

$\frac{6.07536 \times 10^{-6} \text{ cm}^2}{\text{sec}}$