PWR SECONDARY WATER CHEMISTRY STUDY

EPRI NP-516
(Research Project 404-1)

Interim Report

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LEGAL NOTICE

FOREWORD

This interim report describes work done on RP404-1, "PWR Secondary Water Chemistry Study", which is sponsored by the Electric Power Research Institute. This project was initated in order to help resolve problems occurring in recirculating type steam generators in pressured water reactors at commercial nuclear powered utilities. The water chemistry in the secondary systems of these plants, particularly when air and cooling water inleakage occurs, is believed to be an important contributing factor to corrosion damage occurring within steam generators. The purpose of this study therefore is to characterize and better understand secondary system water chemistry under all phases of plant operation and to attempt to relate information obtained to the occurence of steam generator corrosion damage. This will then provide a better technical basis for future corrective measures to avoid such damage. Five nuclear plants are included in the study in order to encompass important system design and site related variables and thereby extend the scope of applicability of program results.

The major significance of findings in the program to date are:

1. Significant levels of chloride can hide out in steam generators, presumably in dry out areas such as support plate crevices. Acid chlorides are believed to be a major contributing cause of steam generator tube denting.
2. Various chemicals present in steam-generator boiler water at startup can return to hideout areas as power levels are increased. This hideout could result in undesirably high levels of aggressive chemicals in crevice areas and should be avoided.
3. Corrosion product input to steam generators in in the order of a half ton a year. Current blowdown systems remove only a small portion of this input.
4. Signigicant progress has been made in this project in modelling the complex behavior of chemicals in steam generators. The results of this work will allow a much better assessment to be made of the benefits and consequences of water treatment additives and inleakage effects.

5. Frequent measurement of chemical and corrosion product species, during various phases of plant operation, and over long time periods, are necessary for adequate characterization of secondary system chemistry.

Work on this project is planned to continue over the next few years. Items expected to be emphasized include effects of cooling towers, demineralizers, secondary system corrective measures to avoid denting, and in-plant model boilers.

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ABSTRACT

Several types of corrosion damage are currently chronic problems in PWR recirculating steam generators. One probable cause of damage is a local high concentration of an agressive chemical even though only trace levels are present in feedwater. A wide variety of trace chemicals can find their way into feedwater, depending on the sources of condenser cooling water and the specific feedwater treatment.

In February 1975, Nuclear Water and Waste Technology Corporation (NWT), was contracted to characterize secondary system water chemistry at five operating PWRs. Plants were selected to allow effects of cooling water chemistry and operating history on steam generator corrosion to be evaluated. Calvert Cliffs 1, Prairie Island 1 and 2, and Surry 2, and Turkey Point 4 were monitored during the program. Results to date in the following areas are summarized:

1) Plant chemistry variations during normal operation, transients, and shutdowns.
2) Effects of condenser leakage on steam generator chemistry.
3) Corrosion product transport during all phases of operation.
4) Analytical prediction of chemistry in local areas from bulk water chemistry measurements.
5) Correlation of corrosion damage to chemistry variation.

ACKNOWLEDGMENT

Without the cooperation of Baltimore Gas and Electric Company, Florida Power and Light Company, Northern States Power Company, and Virginia Electric and Power Company, it would not have been possible to collect the extensive operating plant data presented herein. In particular, we wish to thank Mr. Gary Brobst of the Calvert Cliffs Nuclear Power Plant, Mr. John Linville of the Prairie Island Nuclear Generating Plant, Mr. William Thornton of the Surry Power Station and Mr. John Wade of the Turkey Point Plant for their extensive and continual support during the performance of this study.

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Section 1

INTRODUCTION AND SUMMARY

In the early 1970s, PWR steam generators operating with phosphates experienced extensive tubing corrosion damage. This damage resulted in a significant loss in nuclear plant availability. In addition, requirements for inspection and repair of damage involved significant personnel exposure to radiation. Attempts to alleviate this problem by better control of phosphate chemistry were not successful. As a result, by the fall of 1974 all PWR vendors in the United States recommended that units be converted to all volatile treatment (AVT) for secondary system water chemistry.

To assist in resolving the steam generator problems, the Electric Power Research Institute (EPRI) contracted with Nuclear Water and Waste Technology (NWT) in February 1975 to carry out a PWR Secondary Water Chemistry Study (RP404-1).

Working at five PWR plants, the overall program objectives were as follows:

> "A. Measure those chemical species in PWR secondary systems which may cause corrosion damage to steam generator tubes. In particular, measure all chemical species that interact and control caustic attack as promoted by condenser inleakage from various cooling waters occurring with AVT water chemistry.
>
> "B. Measure those chemical species present in the condenser steam-side environment that result from AVT secondary treatment and which may cause corrosion damage to condenser tubes. In particular, determine the influence of operating history combined with operating transients as they promote aggressive chemical conditions in condensers.
>
> "C. Determine the characteristics and range of secondary system chemistry that are associated with the various operating modes of

> nuclear reactor plants during non-fault conditions. In particular, determine differences in chemistry characteristics as they are affected by prior operation with phosphate water treatment."[1]

Progress on the two-year study performed at 5 operating PWRs was reported to EPRI in seven quarterly reports.[2-8] This interim report presents a summary of program achievements through 1976. More detailed discussions of program accomplishments are available in the quarterly reports. However, the discussion presented herein supercedes those in the quarterly reports which were preliminary in nature.

Section 2
PROGRAM METHODOLOGY

Plant Selection

An evaluation of operating plants was carried out to select five study plants which were optimum for achieving the program technical objectives. Critical considerations in the evaluation included:

1. At least two plants should have been operated only on AVT, and two on phosphate prior to AVT.

2. At least two plants should be seawater or brackish water cooled and two fresh water cooled. A fifth plant preferably should be on fresh water with cooling towers operated at a significant concentration factor.

3. The fresh water coolant must have a relative propensity for forming caustic when concentrated in steam generators as a result of inleakage.

4. Utility management must exhibit a significant interest in the program and commit to cooperate during the plant study.

5. Plants should be of similar vintage so that causes of similarities and differences in performance can be more easily defined.

Of the 28 operating PWRs in the United States,the five selected for the program were:

Plant	Cooling Water	Chemistry	Condensate Cleanup
Calvert Cliffs 1	Brackish	AVT only	Powdered resin 50% deep beds
Prairie Island 1	Fresh*	Phosphate to AVT	None
Prairie Island 2	Fresh*	AVT only	None
Surry 2	Brackish	Phosphate to AVT	None
Turkey Point 4	Sea	Phosphate to AVT	None

* Helper Towers

Calvert Cliffs 1: The Calvert Cliffs Nuclear Power Plant of the Baltimore Gas and Electric Company (BGE) consists of two 840 MWe PWRs with Unit 1 in commerical operation since May 1975. The nuclear steam supply system (NSSS) including steam generators was supplied by Combustion Engineering. The plant is located on the western shore of the Chesapeake Bay halfway between the mouth of the Bay and its headwaters at the Susquehanna River. The mean salinity of the Bay near the plant varies from 17,000 to 18,000 ppm near the bottom and 11,000 to 13,000 ppm in the upper levels.

AVT was used in Unit 1 since startup. No baseline steam generator inspection was performed prior to startup. The first steam generator tube inspection was performed in early 1977.

The Calvert Cliffs Unit 1 secondary system includes a full-flow condensate filtering system that is used with a powdered resin precoat. A deep bed demineralizer system, capable of handling 50% of the condensate flow, also is installed. Since Calvert Cliffs Unit 1 was the first PWR with recirculating steam generators in the United States to have condensate treatment, it was selected as one of the study plants.

Prairie Island 1 and 2: The Prairie Island Nuclear Generating Plant of the Northern States Power Company (NSP) consists of two 530 MWe PWRs with Unit 1 placed in commercial operation in December 1973 and Unit 2 in October 1974. The NSSS and turbine generators were supplied by Westinghouse. The Prairie Island units were the only Westinghouse PWRs operating with all ferrous alloy secondary systems.

The plant is located downstream of Minneapolis - St. Paul on the Mississippi River. The river appeared to be "alkaline forming" based on the fact that excess bicarbonate and alkali ions were available. Although cooling towers are installed, the plant has been operated with once-through flow with the cooling towers operating only to decrease the temperature of the system water before discharge to the river (helper towers).

Unit 1 operated with phosphate in the secondary system between December 1973 and September 1974. Subsequently, the steam generators were eddy current inspected, water lanced and returned to service on AVT.

A normal 100% baseline eddy current inspection was performed on the Unit 2 steam generators prior to startup as then required by Regulatory Guide 1.83[9] (RG 1.83). Although phosphates were used during the hot functional testing, Unit 2 was started on AVT.

The almost identical Prairie Island units offered a close comparison of fresh water cooled plants, Unit 1 having converted from phosphate to AVT and Unit 2 operated with only AVT. Both were selected for study plants in the fresh water cooled category with "alkaline forming" tendencies.

Surry 2: The Surry Power Station of the Virginia Electric and Power Company (VEPCO) consists of two 788 MWe PWRs with Unit 1 placed in commercial operation in December 1972 and Unit 2 in May 1973. The NSSS and turbine generators were supplied by Westinghouse.

The Surry site is located on the James River near its point of entry into Chesapeake Bay. Because of the tidal flows and the James River watershed runoff, the plant cooling water varies during the year from a nearly fresh to a highly saline condition (>6000 ppm).

Both units were operated with phosphate chemistry until the fall of 1974. At that time (December 1974-Unit 1 and September 1974-Unit 2), each steam generator was eddy current inspected, water lanced, and returned to service on AVT.

Both Surry Units had a history of minor steam generator problems on the phosphate chemistry and occasional condenser leaks. Unit 2 was selected as the brackish water cooling water plant for the study in preference to Unit 1 because of a more trouble-free operation up to the time of the decision , better historical records, and an early steam generator inspection schedule (May 1975).

Turkey Point 4: The Turkey Point Plant of Florida Power and Light (FPL) consists of two fossil units and two identical 693 MWe nuclear units. The first nuclear unit, Turkey Point Unit 3, went into commercial operation in December 1972 with Unit 4 going commercial in September 1973. The NSSS and turbine generators were supplied by Westinghouse.

The Turkey Point site is located on the western shore of Biscayne Bay south of Miami. Although the cooling water is recirculated through an extensive system of canals, the chemistry of the water essentially is that of seawater.

Both units were operated with phosphate chemistry until the fall of 1974. At that time (November 1974-Unit 3 and August 1974-Unit 4), each steam generator was eddy current tested, water lanced, and returned to service on AVT.

With seawater cooling, a history of some steam generator problems with phosphate chemistry, and occasional condenser leaks, the Turkey Point nuclear units were of interest to the study. Unit 4 was selected in preference to Unit 3 because the steam generators of Unit 4 had been given a prestartup eddy current examination (Unit 3 had not) and were scheduled for an early inspection after the transition to AVT.

Plant Descriptions

A brief description of the secondary cycle at each plant was included in the first[2] and third quarterlies.[4] Pertinent design characteristics are summarized in Table 2.1. Of particular importance in evaluating program results is that the Prairie Island units are all ferrous systems thereby allowing their operation at pH levels in the 9.4 to 9.6 range. The other units are limited to operation at lower pH because of the copper alloys in the system. This difference has a significant effect on corrosion product transport as discussed in Section IV.

Secondary water chemistry control at each plant generally parallels recommendations of the respective steam generator vendors. Westinghouse and Combustion Engineering (CE) generic specifications for AVT operation are summarized in Tables 2.2 and 2.3. Specifically Westinghouse recommends control of pH, oxygen, hydrazine, specific conductivity, iron, copper and ammonia in the feedwater and pH, free hydroxide and cation conductivity in the steam generator blowdown. CE recommends control of the same feedwater parameters except cation instead of specific conductivity and additionally silica and sodium. In the steam generator blowdown CE recommends control of specific instead of cation conductivity, total hydroxide instead of free hydroxide, and additionally suspended solids and silica.

Instrumentation and Analytical Procedures[2-4]

The instrumentation and analytical procedures for monitoring major specification parameters vary somewhat at the five plants. Installed monitors are summarized in Table 2.4 and analytical procedures in Table 2.5.

A number of chemistry monitoring instruments at each of the plants under study are not operable (Table 2.4) or were not operable during a significant

TABLE 2.1

STUDY PLANT DESIGN CHARACTERISTICS

Plant	Calvert Cliffs	Surry 2	Turkey Point 4	Prairie Island	
				1	2
Mwe (Net)	810	788	693	530	
Start Up (Commercial)	5/75	5/73	9/73	12/73,	12/74
Steam Generators					
Number	2	3	3	2	
No. tubes/generator	8519	3388	3260	3388	
m^2/MW	24	18	18	18	
Total Steam Flow, kg/m	83200	80100	75600	52900	
Months on phosphate	0	23	14	10	0
No. Feedwater Heaters	6	6	6	5	
No. Feedwater Trains	3 Low Pressure 2 High Pressure	2	2	2	
Tubing Materials					
Feedwater Heaters	6 stainless	4 Admiralty 1-90/10 CuNi 1-80/20 CuNi	5 Admiralty 1 Monel	stainless	
Condenser	70/30 CuNi	90/10 CuNi	Al-Brass*	stainless	
Reheaters	90/10 CuNi	90/10 CuNi	90/10 CuNi	carbon steel	

* Air removal section 70/30 CuNi; 1 of 4 water boxes retubed with titanium and 1 with 70/30 CuNi in May 1976.

TABLE 2.2

PWR FEEDWATER SPECIFICATIONS[a]

	Combustion Engineering	Westinghouse
pH	8.8-9.2[b]	8.8-9.2[b]
	9.2-9.5[c]	up to 9.6[c]
O_2, ppb	<10	<5
Abnormal[d]	>10 (4 h)	-
Shutdown	100	-
N_2H_4, ppb	10-50	$[O_2] + 5$
Specific Conductivity, μmhos/cm	-	4
Cation Conductivity, μmhos/cm	<0.5	-
Abnormal	>1.5 (4 h)	-
Iron, ppb	<10	<10
Copper, ppb	<10	<5
Total Silica, as SiO_2, ppb	<10	-
Ammonia, ppm	<1	<0.5
Sodium, ppb	<10	-

a) Tabulated values are for normal operation unless noted otherwise

b) With copper alloys in feedwater heaters, MSR, or condenser

c) With no copper alloys in feedwater heaters, MSR, or condenser

d) Corrective action (or shutdown) recommended within indicated time

TABLE 2.3

PWR RECIRCULATING STEAM GENERATOR WATER QUALITY SPECIFICATIONS[a]

	Combustion Engineering	Westinghouse	
		Fresh Water	Sea or Brackish Water
pH	8.2-9.2	8.5-9.0	8.5-9.0
Abnormal[b]	<7.5 or >9.5 (4 h)	8.5-9.2 (2 w)	8.0-9.2 (2 w)
Shutdown	10.5	<8.5 or >9.4	<8.0 or >9.4
Specific Cond., μmhos/cm	<7	-	-
Abnormal	>15 (4 h)	-	-
Suspended Solids, ppm	<1	-	-
Abnormal	>10	-	-
Free Hydroxide, ppm	-	<0.05	<0.05
Abnormal	-	>0.05 to ≤0.34 (24 h)	>0.05 to ≤0.34 (24 h)
Shutdown	5[c]	>0.34	>0.34
Silica, ppm	<1	-	-
Abnormal	>10 (4 h)	-	-
Cation Cond., μmhos/cm	-	<2.0	<2.0
Abnormal	-	>2 but ≤7 (2 w)	>2 but ≤120 (2 w)
Shutdown	-	>7	>120
Chloride, ppm	-	-	-

a) Parameters are measured in the blowdown and are for normal operation unless otherwise noted.

b) Corrective action (or shutdown) recommended within indicated time.

c) Recommended analytical procedure is for total hydroxide.

TABLE 2.4

CONTINUOUS MONITORS

Instrument	Prairie Island			Surry 2			Turkey Point 4			Calvert Cliffs		
	C	FW	SG	C	FW	SG	C	FW	SG	C	FW	SG
Sodium			0	0*		0*				X	0	
pH	X	X	X	X	X	0*	0	0	0	X	X	X
Conductivity	X	X	X									X
Cation Conductivity	X	X	X	X	X	X*	X*		X	X	X	X
Hydrazine	X	X						X*				
Silica			0				0	0	0			
Oxygen	X	X		X	X		X	0		X	X	

X - functioning

0 - not functioning

* installed during period of program

TABLE 2.5

ANALYTICAL PROCEDURES

Element	Analytical Method	Calvert Cliffs	Prairie Island	Surry	Turkey Point
Ammonia	Specific Ion Electrode		X		X
	Nesslerization	X		X	X
Oxygen	Indigo Carmine		X	X	
	Chemetrics	X			X
Silica	Ammonia Molybdate	X	X		X
Chloride	Ferric Thiocyanate	X		X	
	Mercuric Nitrate Titration		X	X	X
Free Hydroxide	Westinghouse	0	X	X	X
Sodium	Flame Spectrometry	X	X	X	
	Atomic Absorption				X
Iron	Bathophenanthroline	X	X		
	Atomic Absorption		X	X	X
Copper	Neocuproine	X	0		
	Atomic Absorption		0	X	X

0 = Not done

portion of the program. For this reason, heavy reliance was placed on laboratory analyses to determine steam generator and feedwater system chemistry. During steady state operation, the lack of continuous readings for even major system parameters was not necessarily detrimental to obtaining needed program data. However, during transient periods, particularly those associated with condenser leakage, continuous recordings or frequent logging of in-line instrumentation readings were needed to obtain the intensity of data required to accomplish program goals. For this reason additional monitoring equipment was provided to complement available plant instrumentation during intensive study periods.

As noted in Table 2.5, the Westinghouse procedure for free hydroxide is used at 4 of the 5 study plants. The procedure is designed to determine the free hydroxide concentration in a solution containing ammonia or other volatile basic compounds. The procedure requires analysis of two samples. One is analyzed for total hydroxide concentration by acid titration with sample collection and titration under an argon cover gas to minimize carbon dioxide absorption. Back extrapolation from low pH to pH = 7 is employed to determine the end point. The second sample is analyzed for volatile bases such as ammonia, morpholine, hydrazine, etc. The hydroxide contribution of these bases is subtracted from the total hydroxide value determined by the acid titration to determine free hydroxide. Thus, free hydroxide may be defined as the hydroxide associated with non-volatile cations, e.g., sodium. Westinghouse estimates the accuracy of the procedure to be ±0.05 ppm free hydroxide with ammonia pH control and ±0.10 ppm with morpholine or cyclohexylamine pH control.

Calculations were made to determine the accuracy of the technique in the presence of carbon dioxide. Carbon dioxide entering a solution exposed to the atmosphere was shown analytically to have a negligible effect on the measured free hydroxide level.

Other than the analysis for free hydroxide, analytical techniques employed for the determination of other common specification parameters in recirculating PWR systems are relatively standard in the power generation industry.

The automatic analysis systems summarized in Table 2.4 generally will furnish sufficient accuracy for verifying specification conformance. However, such instrumentation, as previously noted, can be out of service for significant lengths of time particularly when operated on the steam generator blowdown. The major difficulty has been the relatively high concentration of insoluble corrosion products which tend to blind electrode systems employed for sodium, oxygen or pH or to foul resin columns or conductivity cells or photometric cells in hydrazine or silica analyzers. Some plants have installed prefilters upstream of their continuous analyzer bank to eliminate this difficulty. However, such filters have, in the absence of constant flow devices, led to gradual reductions in flow rates to the instrumentation bank thereby leading to inaccurate instrument readings. In general, instruments employed at operating plants can be made to function at an adequate level when such instrumentation is given appropriate attention and maintenance.

One recurring question which was encountered during the study was that of the effect of hydrazine, morpholine, or cyclohexylamine on the specific ion technique for determining ammonia concentration. To quantify interference levels, a series of tests was performed in the NWT laboratory. No significant interferences were found at normally encountered concentrations of any of these species. However, high levels (>10 ppm) of cyclohexylamine were found to interfere with the ammonia analysis.[6]

Section 3

PLANT CHEMISTRY

Background Chemistry

Phosphate chemistry specifications evolved with continued plant operating experience. The original Westinghouse specifications recommended phosphate control but did not specify a sodium to phosphate (Na/PO_4) molar ratio. As a result of caustic stress corrosion of some steam generator tubing observed in early 1972, Westinghouse changed their specification to recommend a 2.0 to 2.6 Na/PO_4 molar ratio with phosphate in the range of 10 to 80 ppm on fresh water sites and 25 to 80 ppm on brackish/seawater sites. Because of subsequent wastage attack, a minimum Na/PO_4 ratio of 2.3 was recommended by late 1973 with phosphate control in the 1972 range. As a result, both Surry 2 and Turkey Point 4 were operated first with a Na/PO_4 specification of 2.0 to 2.6 and later with a recommended ratio of 2.3 to 2.6. Prairie Island 1 was operated only in the latter mode prior to the change to AVT.

Blowdown chemistry during phosphate operation for Prairie Island 1, Surry 2 and Turkey Point 4 is shown for one steam generator of each plant in Figures 3.1, 3.2 (a and b) and 3.3 (a and b), respectively. (Data for each steam generator was included in the first quarterly.2) Examination of the three figures indicates the difficulty encountered at these plants in controlling the Na/PO_4 ratio.* These results were developed from measured sodium and phosphate concentrations and were not inferred from pH-phosphate concentration relations. Blowdown phosphate levels also varied at each plant. The phosphate level was maintained at <20 ppm at Prairie Island (Figure 3.1) where the operating limit was 10 to 80 ppm. With an operating limit of 25 to 80 ppm phosphate at seawater plants, Turkey Point 4 averaged 30 to 40 ppm phosphate (Figure 3.3) and Surry 2 approximately 50 ppm (Figure 3.2).

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*Darkened symbols denote that actual data exceed the graph limit.

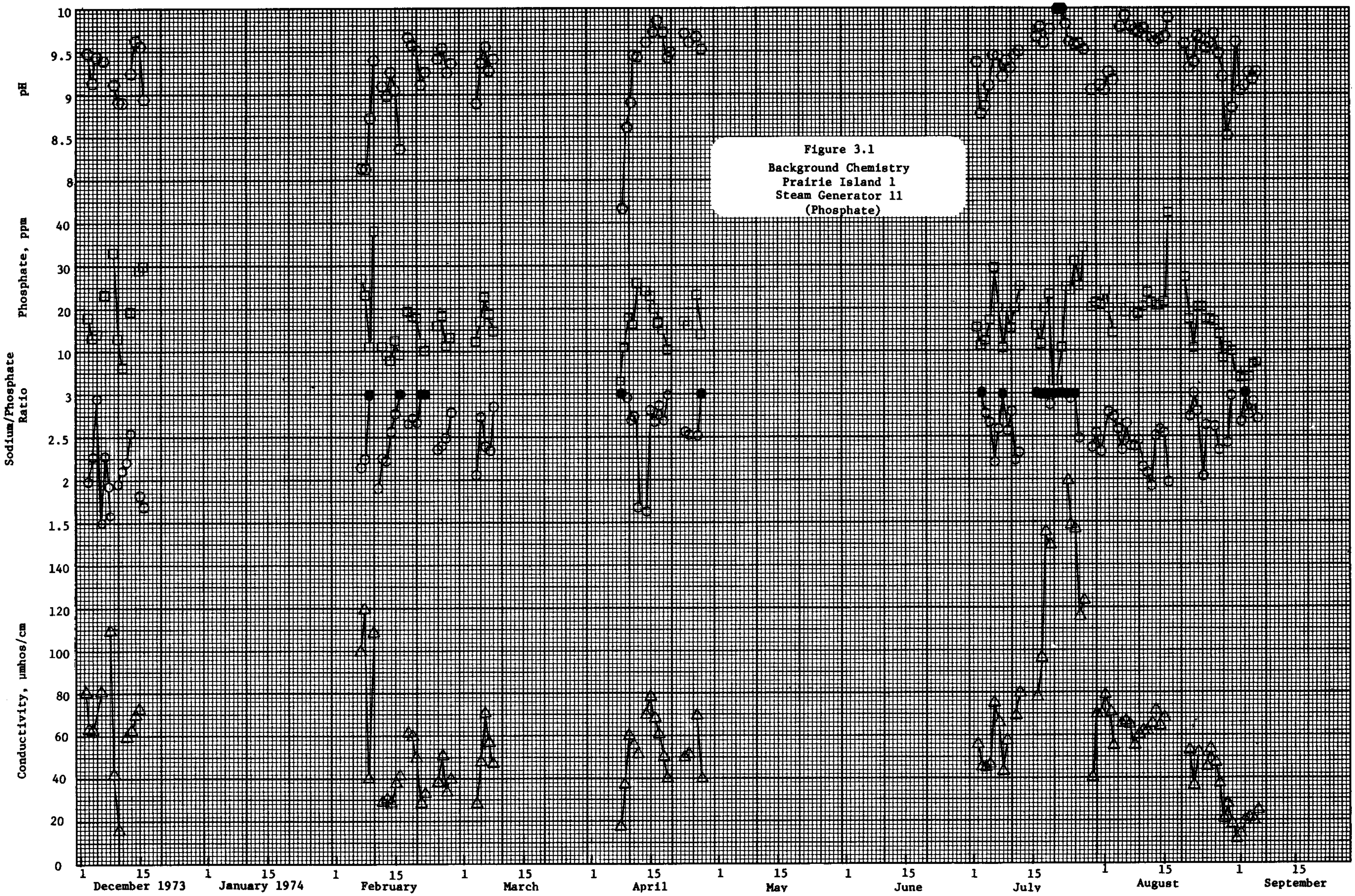


Figure 3.1
Background Chemistry
Prairie Island 1
Steam Generator 11
(Phosphate)

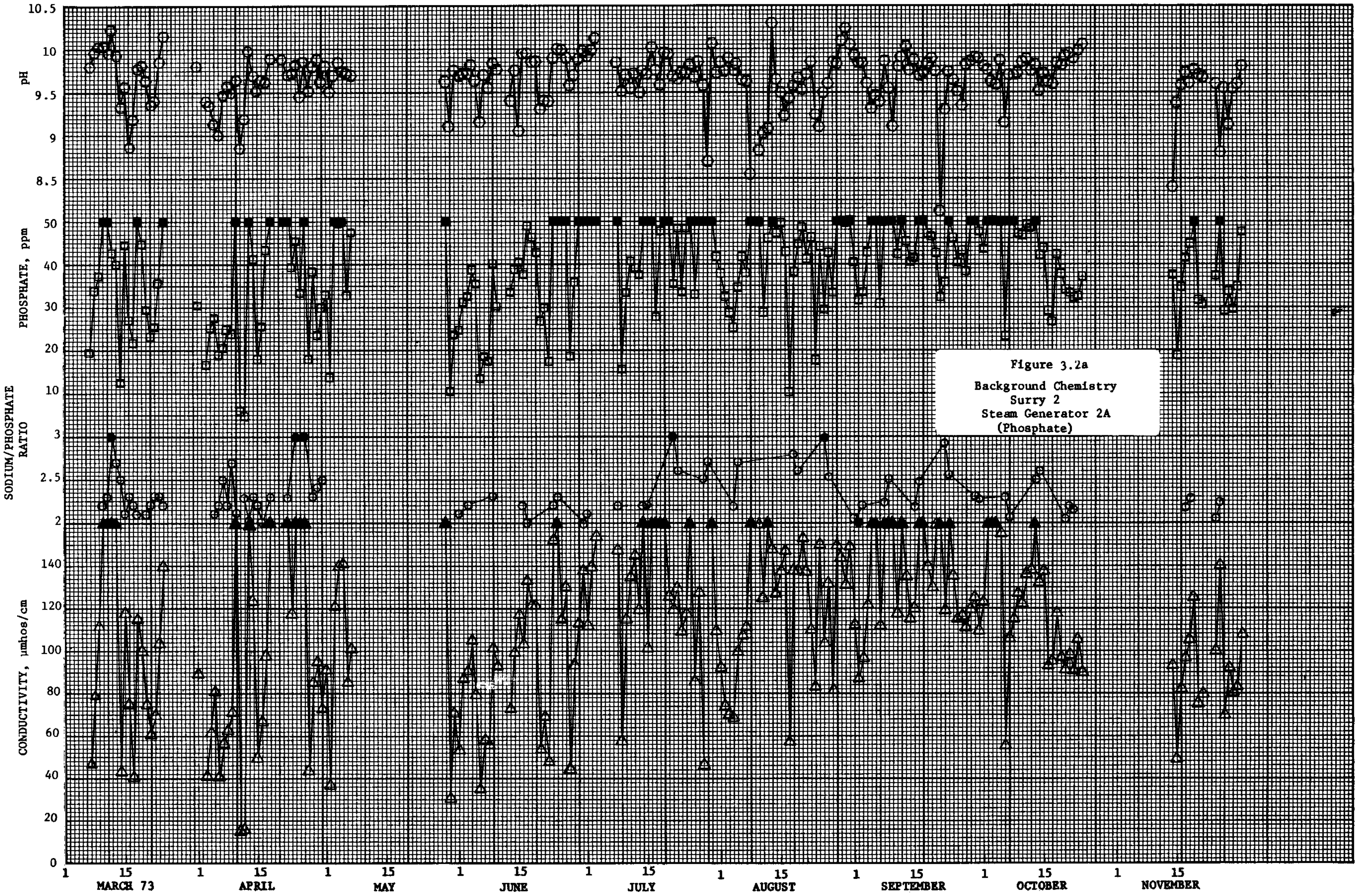


Figure 3.2a

Background Chemistry
Surry 2
Steam Generator 2A
(Phosphate)

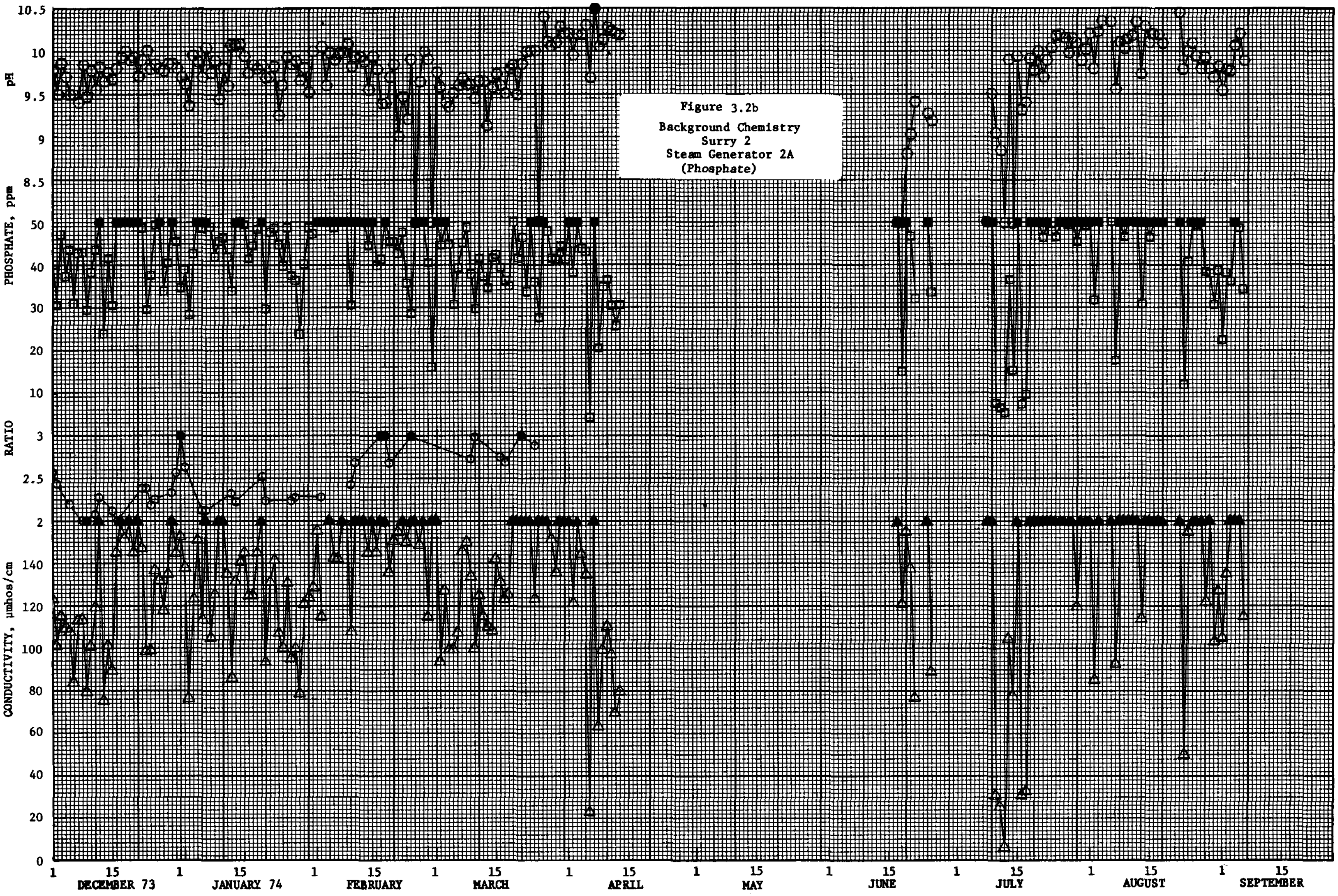


Figure 3.2b
Background Chemistry
Surry 2
Steam Generator 2A
(Phosphate)

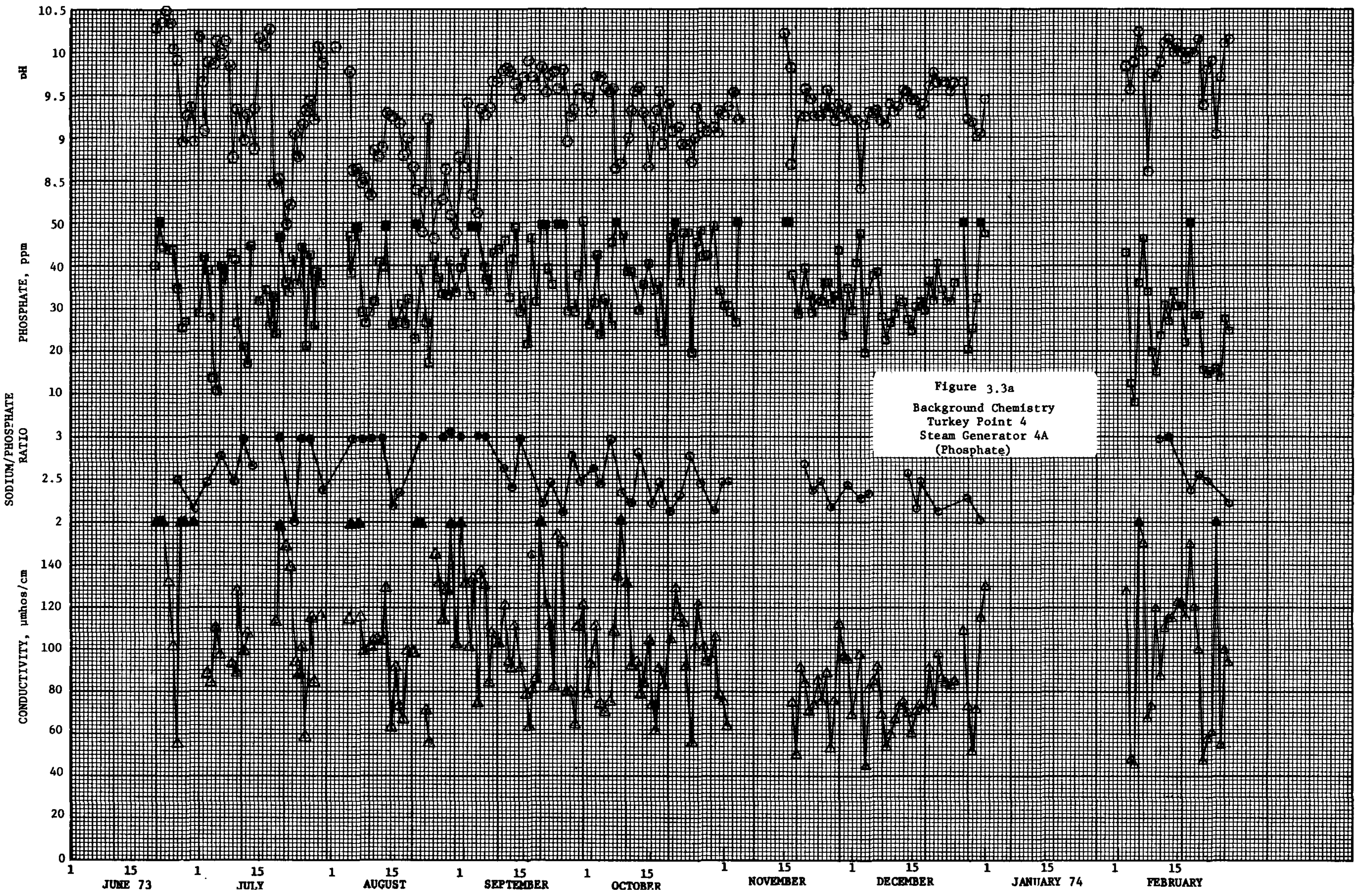


Figure 3.3a
Background Chemistry
Turkey Point 4
Steam Generator 4A
(Phosphate)

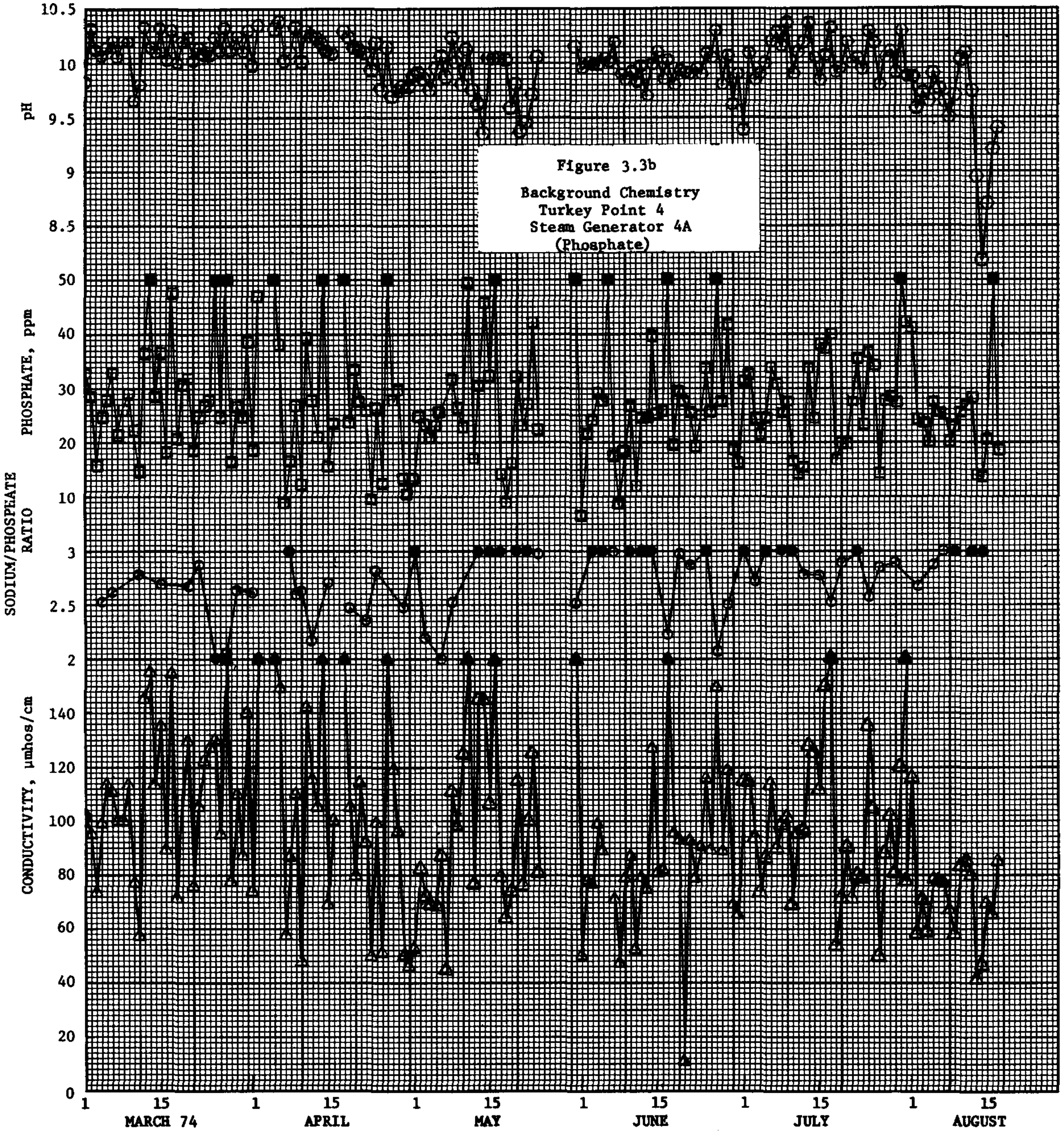


Figure 3.3b

Background Chemistry
Turkey Point 4
Steam Generator 4A
(Phosphate)

Although attempts were made to water lance phosphate sludge from steam generator tube sheets prior to startup with AVT, the phosphate level at Surry 2 remained between 1 and 5 ppm for approximately a week with levels of <0.5 ppm reported during steady operation immediately after this period.

At Turkey Point 4 and Prairie Island 1 the phosphate was <1 ppm within 2 and 3 days, respectively, of the conversion to AVT and decreased to 0.1 ppm within a month at Prairie Island 1. Turkey Point phosphate analyses were stopped after 2 days.

Chemistry histories were collected for each plant with the goal of relating failure mode and extent after conversion to AVT to phosphate chemistry variations. Unfortunately, it was not possible to achieve this goal because of the overriding impact of the denting failure mode at Surry and Turkey Point.

A number of possibilities have been discussed in the industry relative to the influence of operation with phosphates on the types of failures that have been observed. Westinghouse has taken the position that at least one mode of failure, i.e., denting, has as a necessary precursor the presence of phosphate. Another school of thought suggests that the changeover process itself is critical to the initiation and propagation of denting. Until the mechamisms of each observed failure mode have been established, determining the influence of phosphate operational history on failure mode and extent is not felt to be achievable.

Chemistry During Study

Chemistry log sheets detailing normally performed chemical analyses on steam generator blowdowns were obtained routinely from each plant. Major system parameters were selected for each plant to reflect variations encountered during normal operation and those attributable to such events as condenser cooling water leakage. Data on the major parameters for all the steam generators at each participating plant were presented in graphical form in the quarterly reports.[2-8] General observations at each plant are discussed below.

Calvert Cliffs: Steam generator blowdown conductivity, sodium concentration, and pH for Calvert Cliffs steam generator 11 are shown in Figure 3.4 for July through December 1976. This period is representative of normal variations encountered at Calvert Cliffs during the program. As shown, pH generally varied between 8.2 and 8.8 with minor pH depressions evident on several occasions. Such depressions can either result from effects of cooling water inleakage, temporary loss of ammonia or hydrazine feed, or insertion of condensate demineralizers with removal of ammonia by hydrogen form cation resin. Cooling water leakage and demineralizer insertion effects are discussed in Section VI. During normal operation specific conductivity varies between approximately 2 and 4 μmhos/cm. Sodium generally remains below 25 ppb with intermittent spikes resulting from either insertion of condensate demineralizers with attendant elution of sodium from previously exposed resins or direct cooling water inleakage. Reference should be made to Section VI for further clarification of the sodium variations.

Prairie Island 1: Variations of cation conductivity, free hydroxide concentration, and pH on steam generator 11 at Prairie Island 1 are presented in Figure 3.5 for May through October 1976. As shown, pH generally varied between 9.2 and 9.5. This all ferrous plant is operated at significantly higher pH than Calvert Cliffs 1, Surry 2 or Turkey Point 4 which have copper alloys in the feedwater system and condensers. The free hydroxide variation is felt to result from analytical inaccuracies rather than an actual variation in free hydroxide concentration. Emphasis was initially placed on free hydroxide as a major control parameter relative to steam generator corrosion because of the hypothesized likelihood of caustic associated stress corrosion cracking of the Alloy 600 tubing. Cation conductivity normally remains below 1 μmhos/cm except during startup periods when some return of phosphate, and also cooling water associated anionic species occur. The presence of significant quantities of carbon dioxide also is

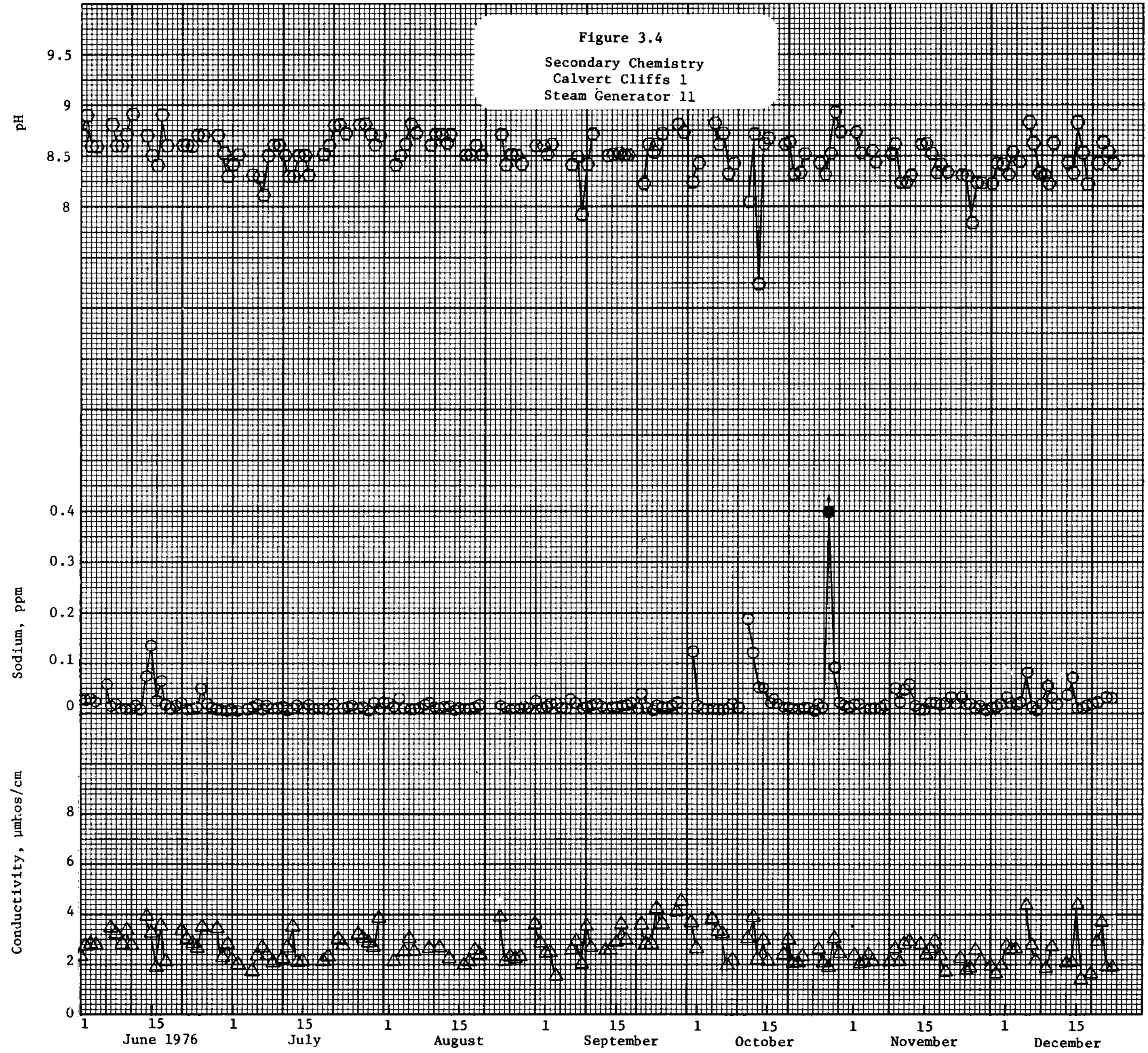


Figure 3.4
Secondary Chemistry
Calvert Cliffs 1
Steam Generator 11
pH
9.5
9
8.5
8
Sodium, ppm
0.4
0.3
0.2
0.1
0
Conductivity, µmhos/cm
8
6
4
2
0
1
15
June 1976
1
15
July
1
15
August
1
15
September
1
15
October
1
15
November
1
15
December

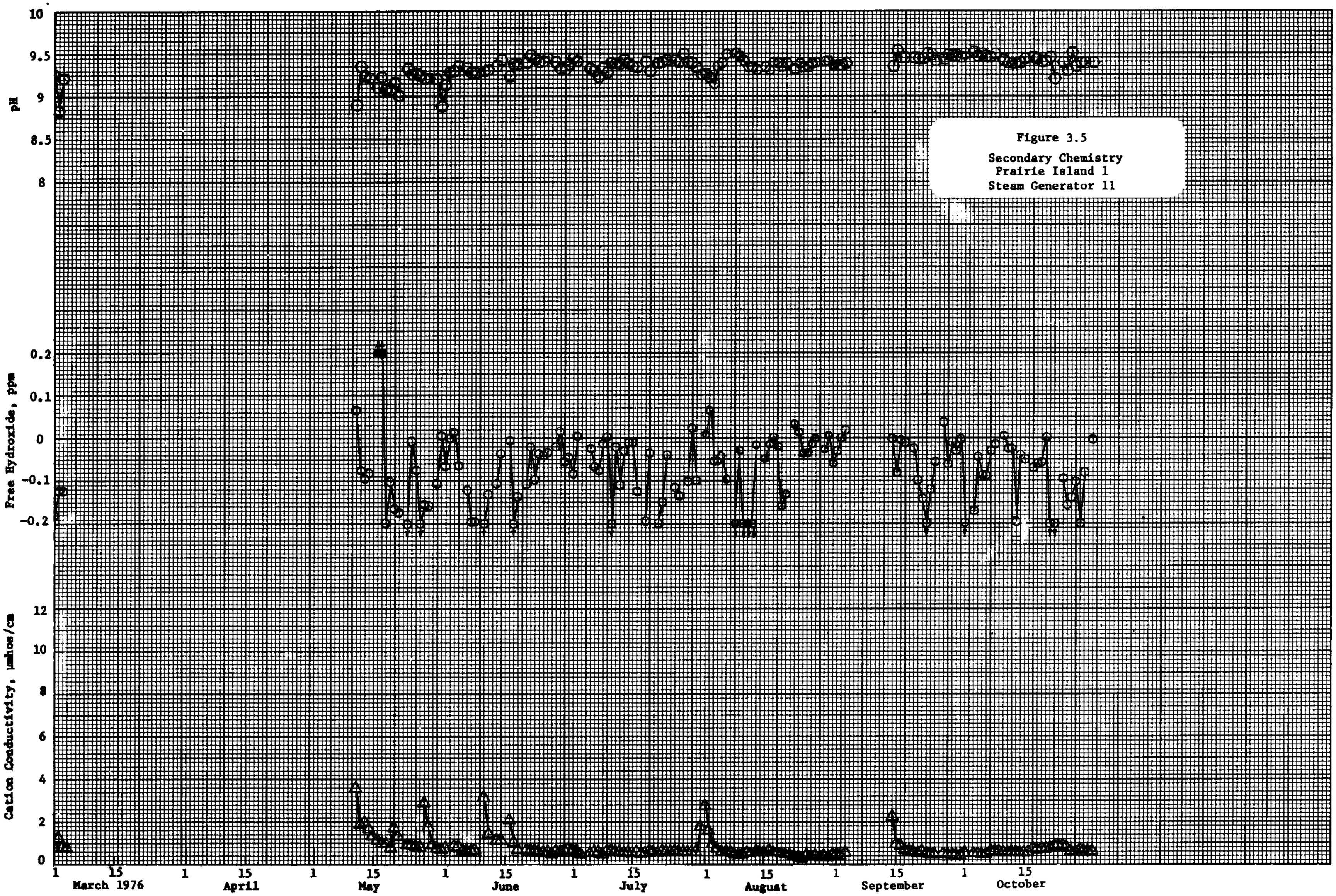


Figure 3.5

Secondary Chemistry
Prairie Island 1
Steam Generator 11

encountered during such periods thereby further contributing to increased levels of cation conductivity.

Carbon dioxide enters the system when it is vented to the atmosphere during shutdowns or via air inleakage during normal operation. The equilibrium carbon dioxide concentration in water exposed to the atmosphere is on the order of 0.5 ppm. Prior to establishing steam seals and operating the air ejectors during a startup, concentrations throughout the feedwater system will approach this level. As discussed in Section VII (Modeling), carbon dioxide is predicted to volatilize in the steam generators and be transported throughout the system, where it can lead to significant pH depressions below those corresponding to the volatile treatment chemical concentration. As such, increased corrosion rates of system materials result.

Prairie Island 2: Steam generator 21 chemistry at Prairie Island 2 is shown in Figure 3.6 for March through October 1976. Chemistry variations at Prairie Island 2 are similar to those noted and discussed above for Prairie Island 1. No significant differences between plants are observed in the three selected steam generator chemistry monitored parameters even though Prairie Island 1 operated initially for approximately 6 months on phosphates.

Surry 2: Steam generator 2A chemistry at Surry 2 is shown in Figure 3.7 for March through September 1976. At this brackish water cooled plant, chloride was selected as an additional indicator of cooling water inleakage. The relative frequency of cooling water leaks is evidenced by the periods of significant chloride concentrations, e. g., August and September 1976. Concurrent with the increases in chloride concentration are increases in cation conductivity and generally decreases in pH. As discussed in Section VI on condenser leakage effects, the observations at Surry are consistent with observations at Calvert Cliffs 1 and Turkey Point 4. In addition, these variations in bulk water chemistry are consistent with those suggested by analytical models developed during this program as discussed in Section VII. The degree of pH depression (Figure 3.7) does

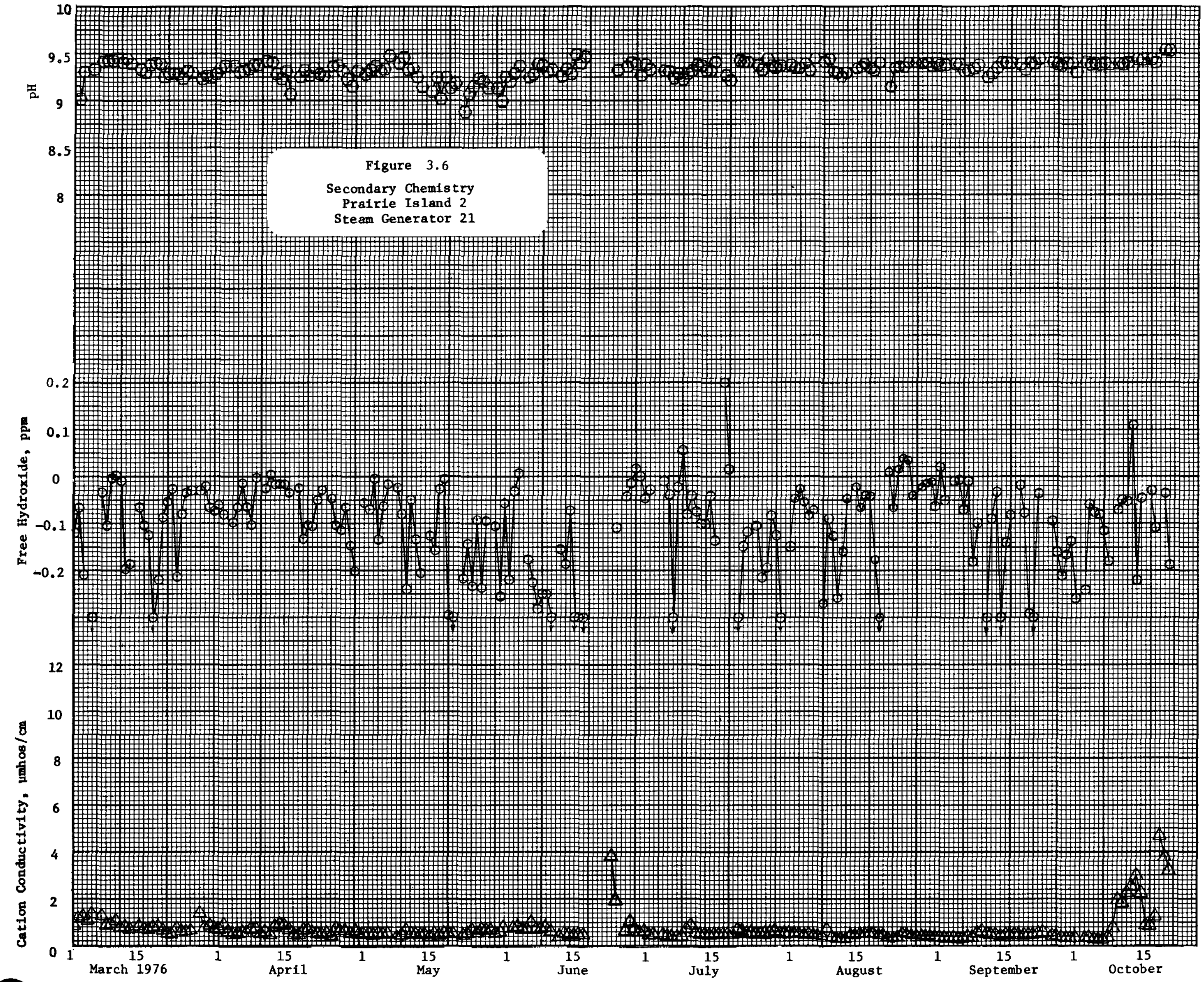


Figure 3.6

Secondary Chemistry
Prairie Island 2
Steam Generator 21

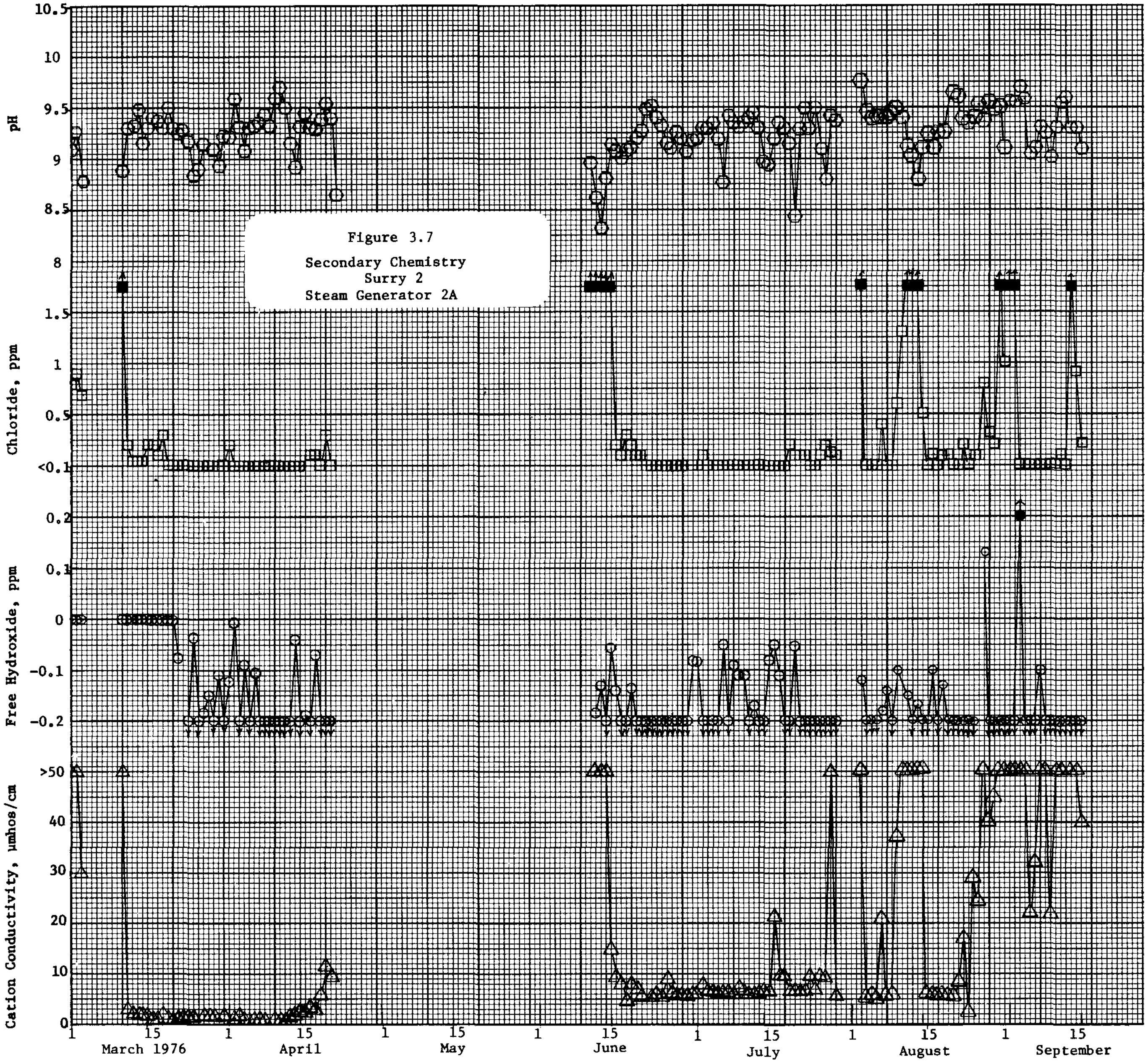


Figure 3.7

Secondary Chemistry
Surry 2
Steam Generator 2A

not necessarily correlate with the absolute level of chloride concentration observed in the blowdown in that feed rate of the volatile chemical additives such as cyclohexylamine is increased during leakage periods. This partially compensates for the formation of acidic species which occurs with precipitation of magnesium hydroxide or silicate.

Turkey Point 4: Chemistry results for steam generator 4A blowdown at Turkey Point 4 are presented in Figure 3.8 for March through October 1976. Similar parameters were selected for Turkey Point 4 as for Surry 2 to reflect the variations in general chemistry. As shown, blowdown pH is generally maintained between 8.5 and 9.0. pH depressions are observed with increases in chloride concentration which result from condenser cooling water inleakage. It should be noted that the general level of cation conductivity is relatively similar to that observed at Surry 2 in the absence of condenser leakage; however, the magnitude and duration of the cation conductivity increases appear generally less severe than at Surry 2. Variations in pH which result from the effects of condenser leakage or variations in volatile chemical addition rates also appear to be less significant than at Surry 2. The variation of free hydroxide concentration between approximately -0.15 to +0.15 ppm reflects what is considered to be the accuracy of the analytical procedure.

Steam Generator Differences: For the sake of brevity, steam generator chemistry for only one generator at each study plant has been included in this report. However, it should be recognized that chemistry differences between generators were observed on numerous occasions during the study. Differences between generators can occur for a variety of reasons including the following:

1. Primary to secondary system leaks.
2. Inequality of volatile chemical feed rates.
3. Non-uniform distribution of pumped forward heater drains.
4. Variations in blowdown flow rate between generators.
5. Treatment differences during layup.

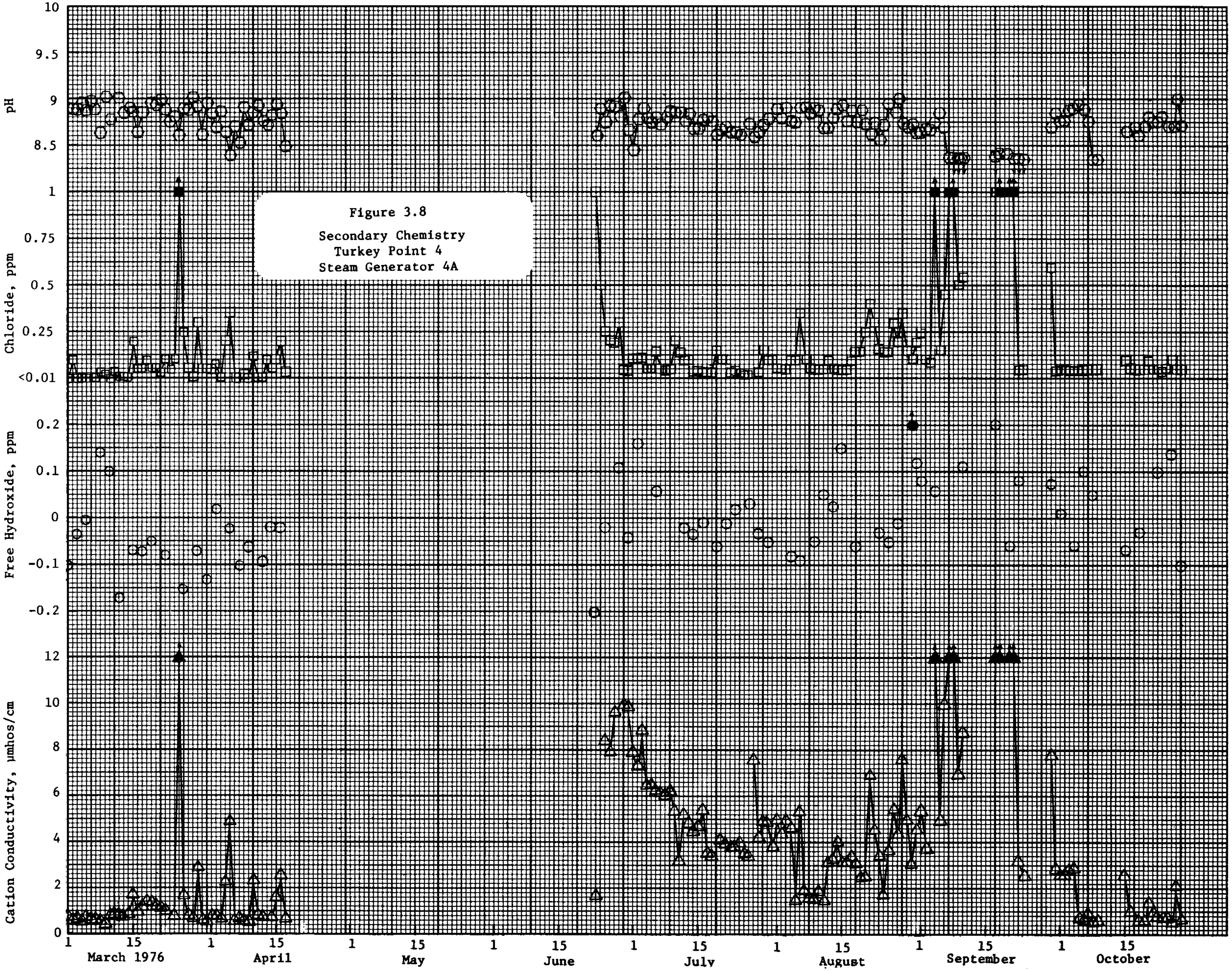


Figure 3.8

Secondary Chemistry
Turkey Point 4
Steam Generator 4A

6. Operational differences during startup.
7. Variations in carryover.

A discussion of observed differences at several plants will be found in the quarterly reports.[2-8] Emphasis was not placed on delineating reasons for the differences during this program.

Section 4

CORROSION PRODUCT TRANSPORT

Methodology

Recognizing that it was not possible to obtain sufficiently accurate corrosion product concentration data from operating plants employing grab sampling and conventional analytical techniques, nine sampling modules each containing two integrated sample collection systems were designed and fabricated for installation at the study plants. The sample collection system design is shown in Figure 4.1. A Millipore® 0.45 micron membrane was used to collect filterable species from a continuous sample flow of approximately 100 cc/min over periods of 1 to 3 days. Three cation ion exchange membranes were inserted in the Millipore holder beneath the filter membrane to collect soluble cationic species and possibly colloidal species. Modules were operated by plant personnel with samples shipped to the NWT laboratory on approximately a once per month basis. Membranes were dissolved using perchloric and hydrochloric acid over a period of several days with final sample analysis by atomic absorption techniques.

The sample collection methods allowed long term averaging of corrosion product concentrations in the feedwater system and steam generator blowdown thereby providing a firm basis for performing mass balances around specific components such as the steam generator. In addition, it was possible to identify major sources of corrosion products within the feedwater system. Two modules were installed at Surry 2, Turkey Point 4, and Calvert Cliffs and three modules at the Prairie Island site. At Calvert Cliffs and Turkey Point 4, two steam generator blowdowns, feedwater, and condensate were monitored. At Surry 2, samplers were operated on two generator blowdowns with the other two varied between the condensate, high pressure heater drains and feedwater.

At Prairie Island, feedwater, condensate, and a single steam generator blowdown were monitored at each plant during initial periods of the program. During latter periods of the program, all six sampling systems were employed

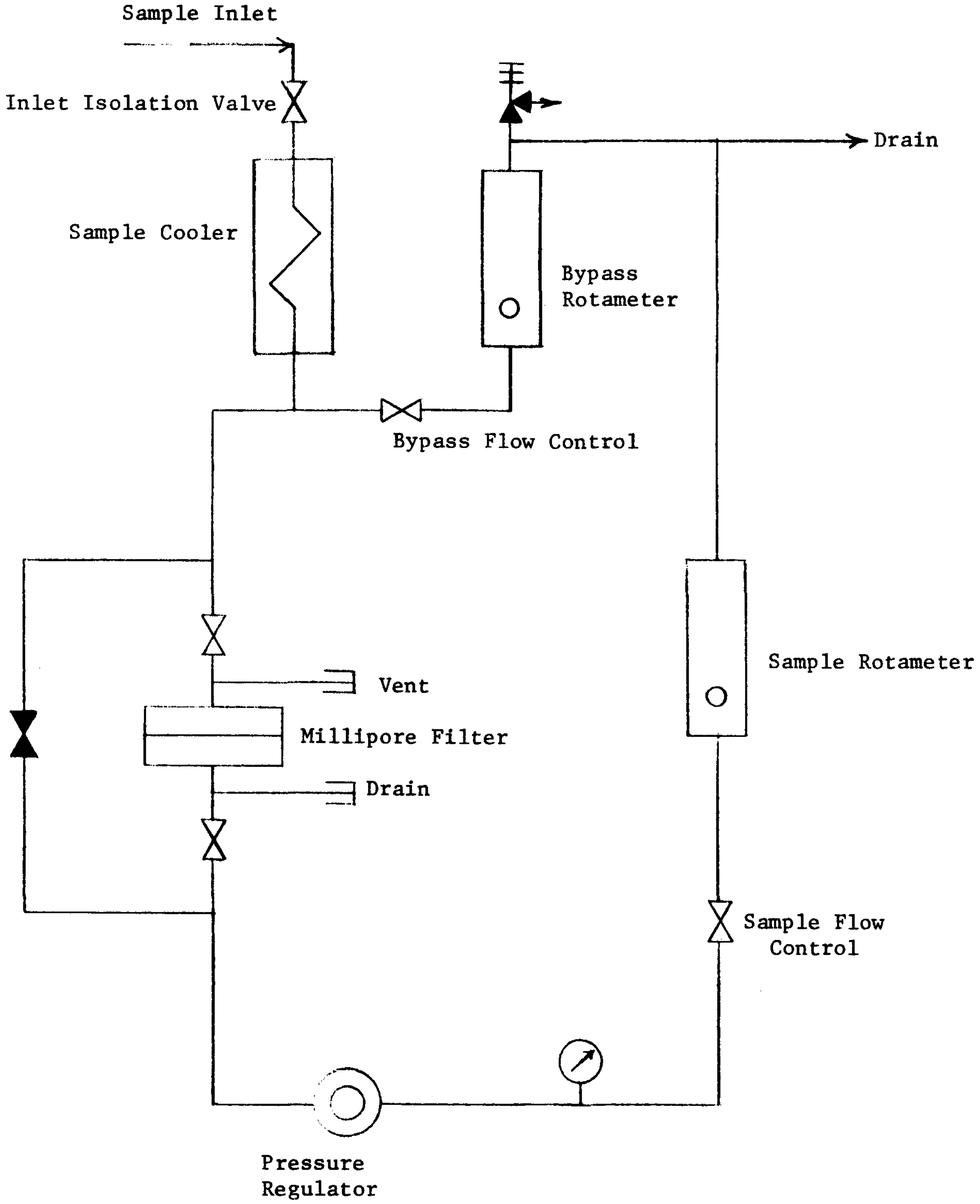


Figure 4.1. Sampling System Schematic

on a single unit, monitoring two steam generator blowdowns, feedwater, condensate, moisture separator drains, and high pressure heater drains. This allowed more detailed delineation of corrosion product sources to be developed for Prairie Island 1 and 2.

Total corrosion product transport past a specific location in the secondary system of each plant was developed based on the corrosion product concentration results, system flow rates (power) during the period of sampling, and the total sampling time. For example, if the condensate flow rate during the sampling period was 10^7 kilograms/h, the average corrosion product concentration was 10 ppb, and the time of sampling was 100 hours, 10 kilograms of that corrosion product would have been transported via the condensate.

Corrosion Product Concentrations

Detailed corrosion product concentration results for each plant were presented and discussed in the quarterly reports.[2-8]

Representative total iron concentrations at Prairie Island 2 and Turkey Point 4 in the condensate, feedwater, and steam generator blowdown are shown in Figures 4.2 and 4.3, respectively. Copper concentrations at Surry 2 and Turkey Point 4 in the condensate and feedwater are shown in Figures 4.4 and 4.5, respectively. Each symbol represents a single datum with the length of the horizontal line through that datum representing the time period over which the average concentration applies.

Average corrosion product concentrations for each plant during normal base load operation are shown in Table 4.1. These results were obtained from selected data when each plant was operated at full power and no known transients occurred. Generally, from 80 to 95% of the corrosion products existed in a filterable form. Average concentrations over the total study period including all monitored transients are given in Table 4.2.

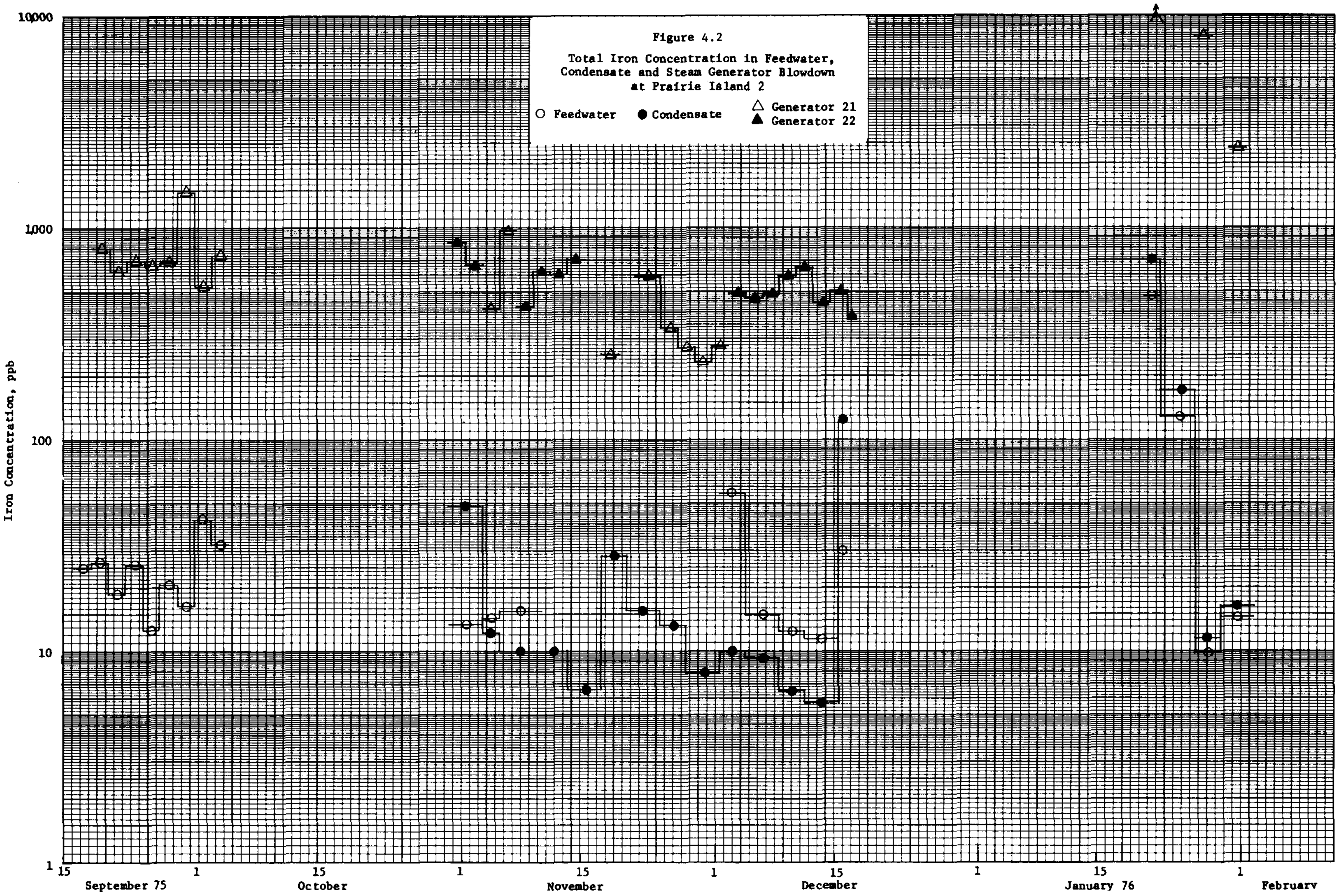


Figure 4.2

Total Iron Concentration in Feedwater, Condensate and Steam Generator Blowdown at Prairie Island 2

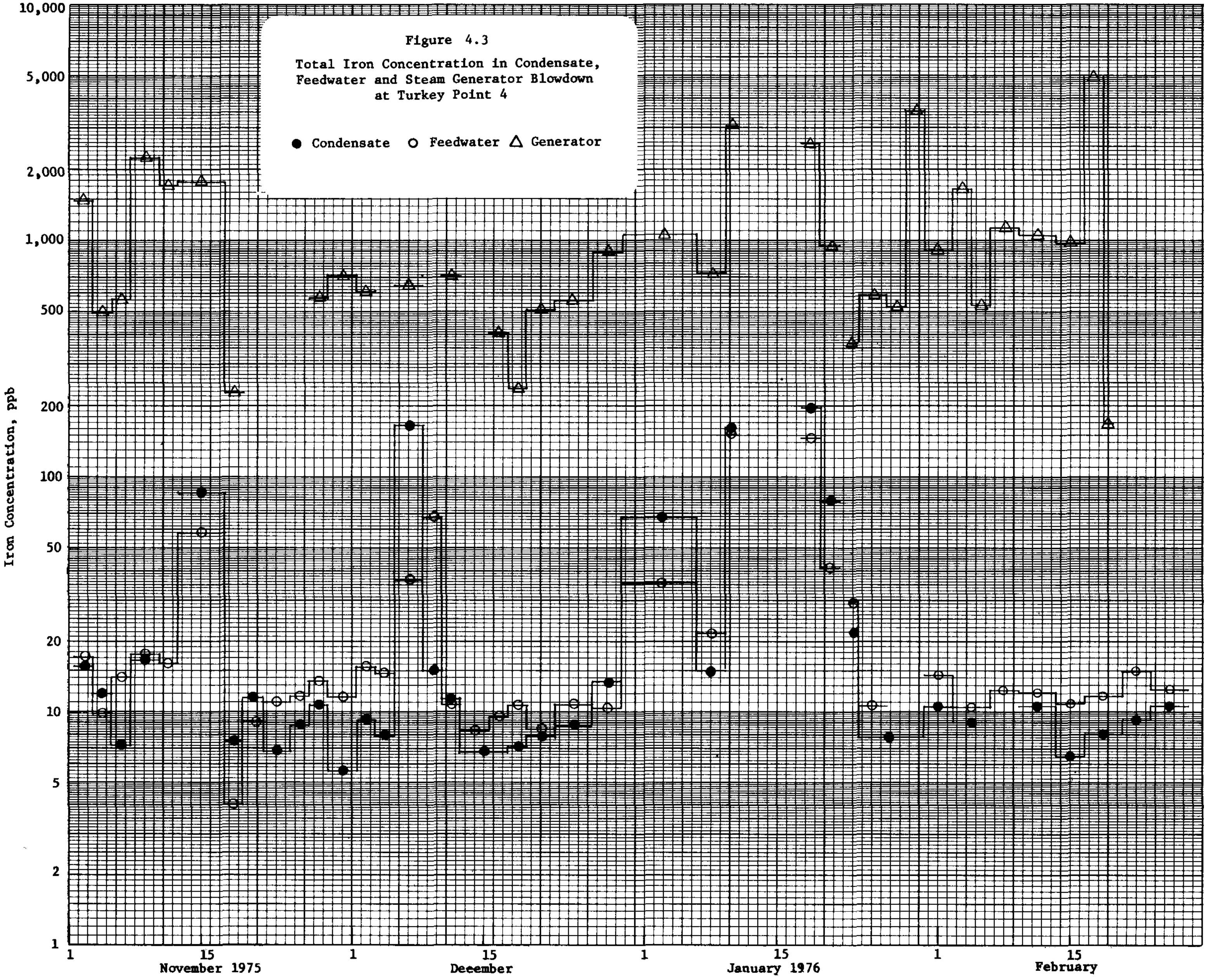


Figure 4.3

Total Iron Concentration in Condensate, Feedwater and Steam Generator Blowdown at Turkey Point 4

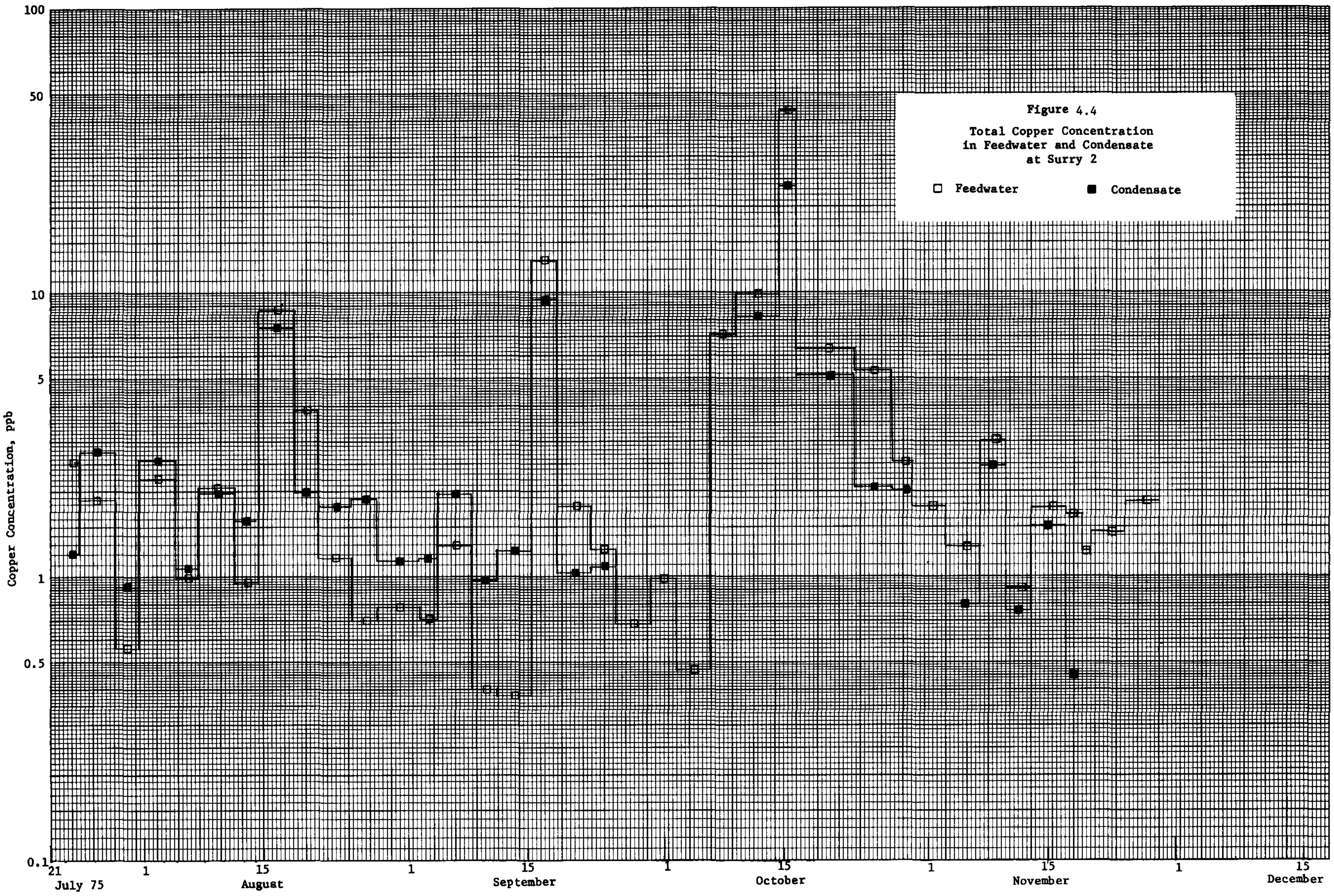


Figure 4.4

Total Copper Concentration in Feedwater and Condensate at Surry 2

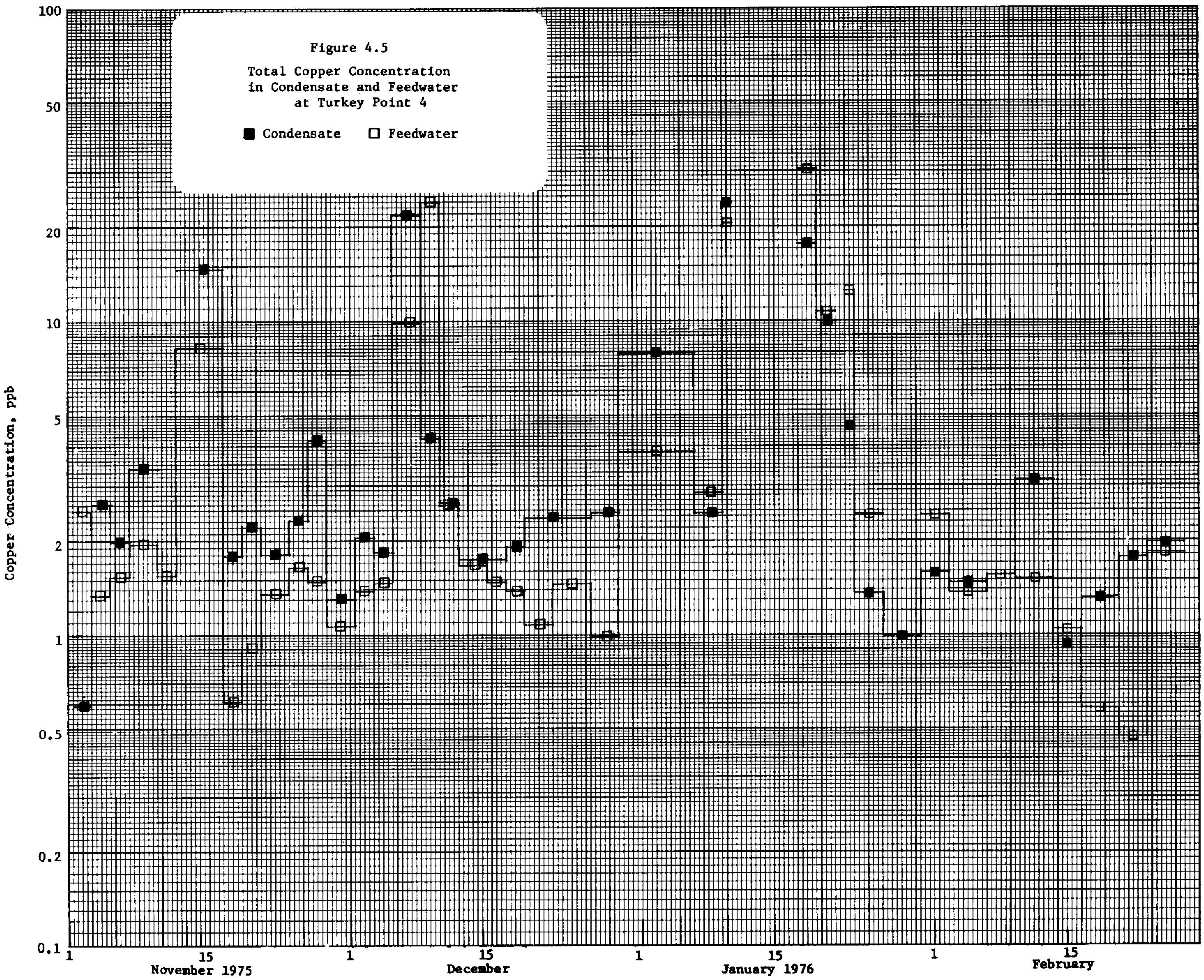


Figure 4.5

Total Copper Concentration in Condensate and Feedwater at Turkey Point 4

TABLE 4.1

AVERAGE CORROSION PRODUCT CONCENTRATIONS DURING NORMAL BASE LOADED OPERATION

ppb (sampling hours)

Station		Condensate	Feedwater	Steam Generator Blowdown	High Pressure Drain	Moisture Separator Drain
Calvert Cliffs 1	Iron	15 (1020)	17 (1020)	310 (680)	*	*
	Copper	0.8 "	0.6 "	13 "	*	*
	Nickel	0.5 "	0.6 "	12.6 "	*	*
Prairie Island 1	Iron	11.2 (1640)	12.1 (1930)	650 (1740)	*	*
	Copper	*	*	*	*	*
	Nickel	ID**	ID	ID	ID	ID
Prairie Island 2	Iron	10.2 (2550)	11 (2580)	1420 (2360)	7.1 (2570)	22.1 (2080)
	Copper	*	*	*	*	*
	Nickel	0.1 "	0.3 "	15.6 (1170)	0.2 "	0.5 "
Surry 2	Iron	11.3 (1390)	8 (3010)	225 (2320)	9.4 (3030)	*
	Copper	1.6 "	1.45	11 "	1.0 "	*
	Nickel	0.2 (390)	0.3	17.8 (1170)	0.4 "	*
Turkey Point 4	Iron	10.5 (2390)	11.7 (2390)	1110 (2050)	*	*
	Copper	1.9 "	1.5 "	31 "	*	*
	Nickel	0.2 "	1.7 "	80 "	*	*

* Not Applicable

**ID - Insufficient Data

TABLE 4.2

AVERAGE CORROSION PRODUCT CONCENTRATIONS INCLUDING ALL PHASES OF OPERATION

ppb (sampling hours)

Station		Condensate	Feedwater	Steam Generator Blowdown	High Pressure Drain	Moisture Separator Drain
Calvert Cliffs 1	Iron	25.1 (1310)	23.6 (1310)	600 (1080)	*	*
	Copper	1.2 "	1.0 "	13.2 "	*	*
	Nickel	1.3 "	1.0 "	14 "	*	*
Prairie Island 1	Iron	15.5 (2420)	14.9 (2490)	870 (2480)	*	*
	Copper	*	*	*	*	*
	Nickel	0.1 (230)	0.2 (230)	15.4 (190)	*	*
Prairie Island 2	Iron	21.0 (4090)	18.0 (4150)	1520 (2840)	7.1 (2970)	22.2 (2950)
	Copper	*	*	*	*	*
	Nickel	0.1 (2950)	0.3 (2980)	16.2 (1380)	0.2 (2970)	0.5 (2950)
Surry 2	Iron	18.0 (2370)	15.2 (4530)	500 (4600)	14.3 (4480)	*
	Copper	2.5 "	3.0	74 "	3.6	*
	Nickel	0.2 (390)	0.7 (4470)	32 (2680)	0.9	*
Turkey Point 4	Iron	19.3 (4530)	19.5 (4530)	1400 (4000)	*	*
	Copper	3.2 "	2.7 "	49 "	*	*
	Nickel	0.3 (3060)	2.1 (3060)	92 (2760)	*	*

* Not Applicable

As expected, overall average concentrations are significantly greater than those observed during periods of normal base load operation reflecting the significant changes in corrosion product transport which result with variations in plant power. Although the corrosion product concentration data were employed primarily to develop mass transport relations around the secondary system, some insight into the impact of alternate material selections or operating chemistry can be obtained from review of Table 4.2. For example, feedwater iron concentration at Calvert Cliffs is significantly greater than at the other plants. This appears to have resulted from operation of the feedwater system at a lower average pH than employed at the other plants. Another interesting comparison is the relatively high concentration of nickel in the feedwater at Turkey Point 4 compared to the other plants. This appears to result from corrosion of the Monel (70/30 nickel copper) last stage feedwater heater. Prairie Island 1 and 2 have stainless steel feedwater heaters and condenser tubing which appears to contribute only minimal nickel input rates compared to those observed at the other plants. At Surry 2, the nickel input results from corrosion of the 90/10 copper nickel condenser, and 90/10 and 80/20 copper nickel feedwater heaters. Some input from the 90/10 copper nickel reheater tubing also occurs. At Calvert Cliffs, the nickel input results from corrosion of the 70/30 copper nickel condenser and 90/10 reheater. As discussed below, the mass transport relations present a clear insight into the impact of alternate materials selection on corrosion product transport throughout the secondary system.

Mass Transport Evaluation: Steam Generator Sludge Buildup

Feedwater iron input to the steam generator and the iron removal via blowdown from the steam generator at the five study plants are shown in Figures 4.6 through 4.10. Transport results for iron, copper, and nickel are summarized for each plant in Table 4.3. Similar results are given in Table 4.4 normalized to individual plant power rating. As can be seen, the feedwater iron transport varied from approximately 50 to 130 grams/h with the efficiency of the steam generator blowdown for removal of iron

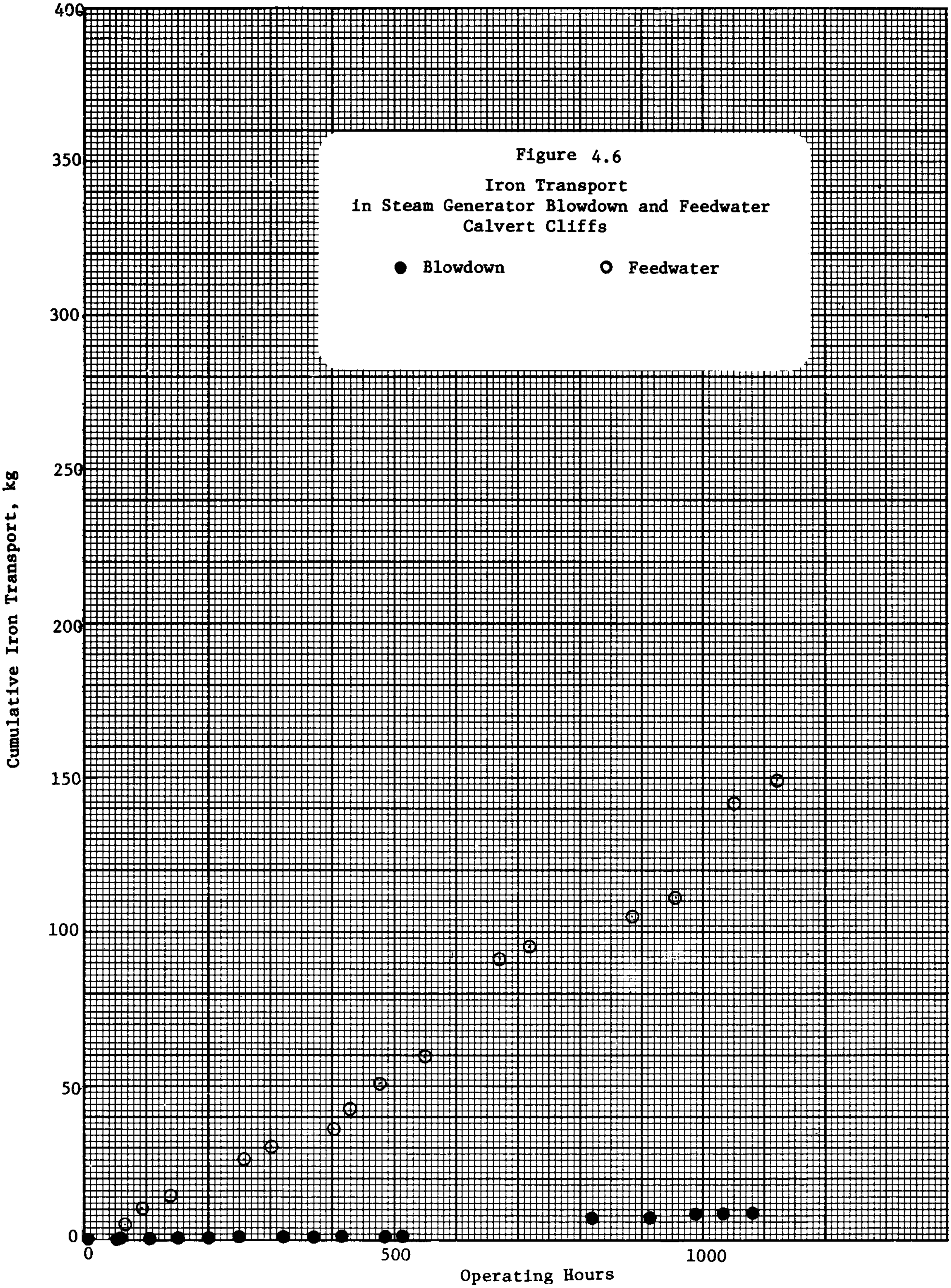


Figure 4.6
Iron Transport
in Steam Generator Blowdown and Feedwater
Calvert Cliffs
● Blowdown
O Feedwater
400
350
300
250
200
150
100
50
0
Cumulative Iron Transport, kg
0
500
1000
Operating Hours

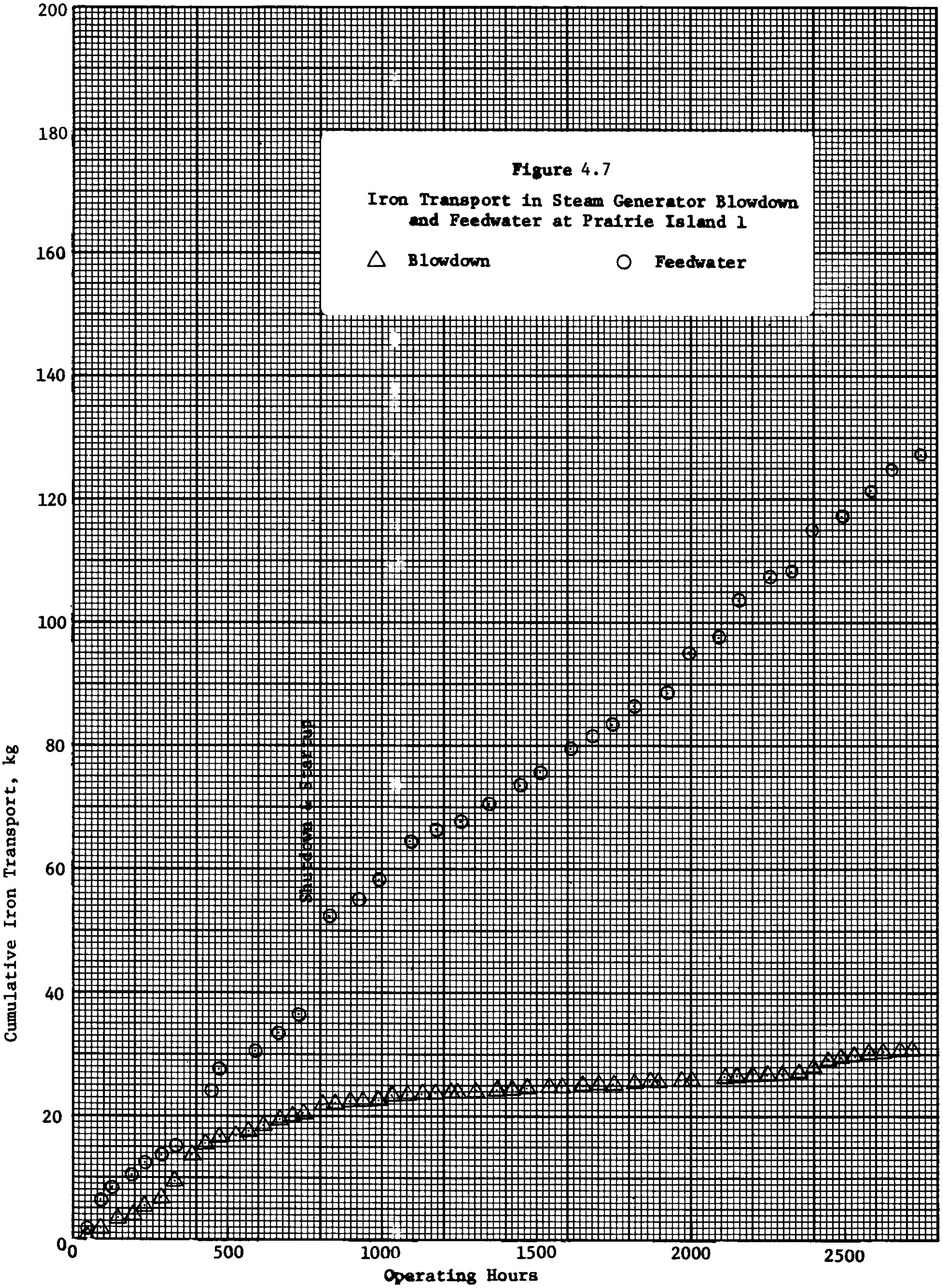


Figure 4.7

Iron Transport in Steam Generator Blowdown and Feedwater at Prairie Island 1

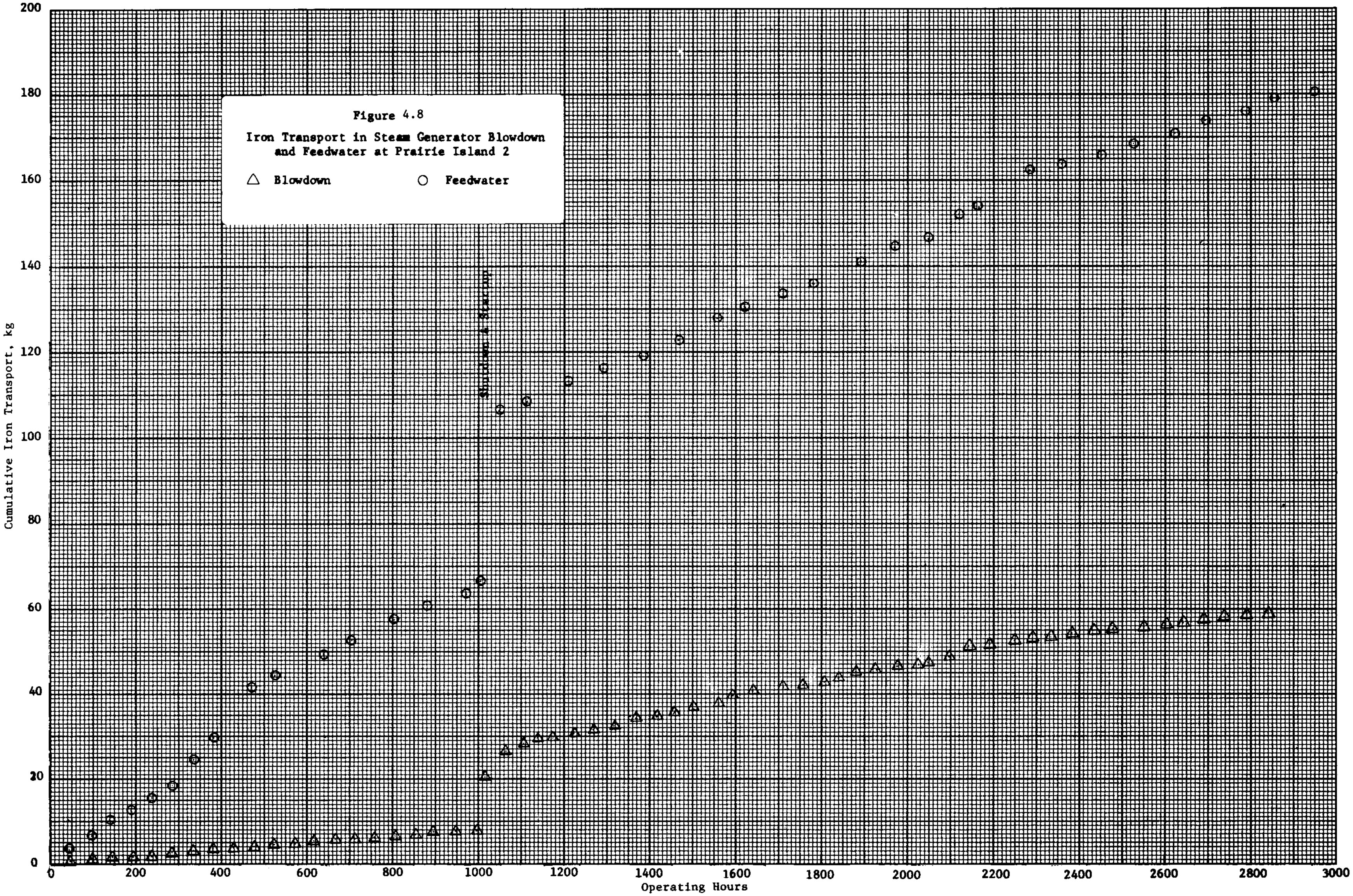


Figure 4.8

Iron Transport in Steam Generator Blowdown and Feedwater at Prairie Island 2

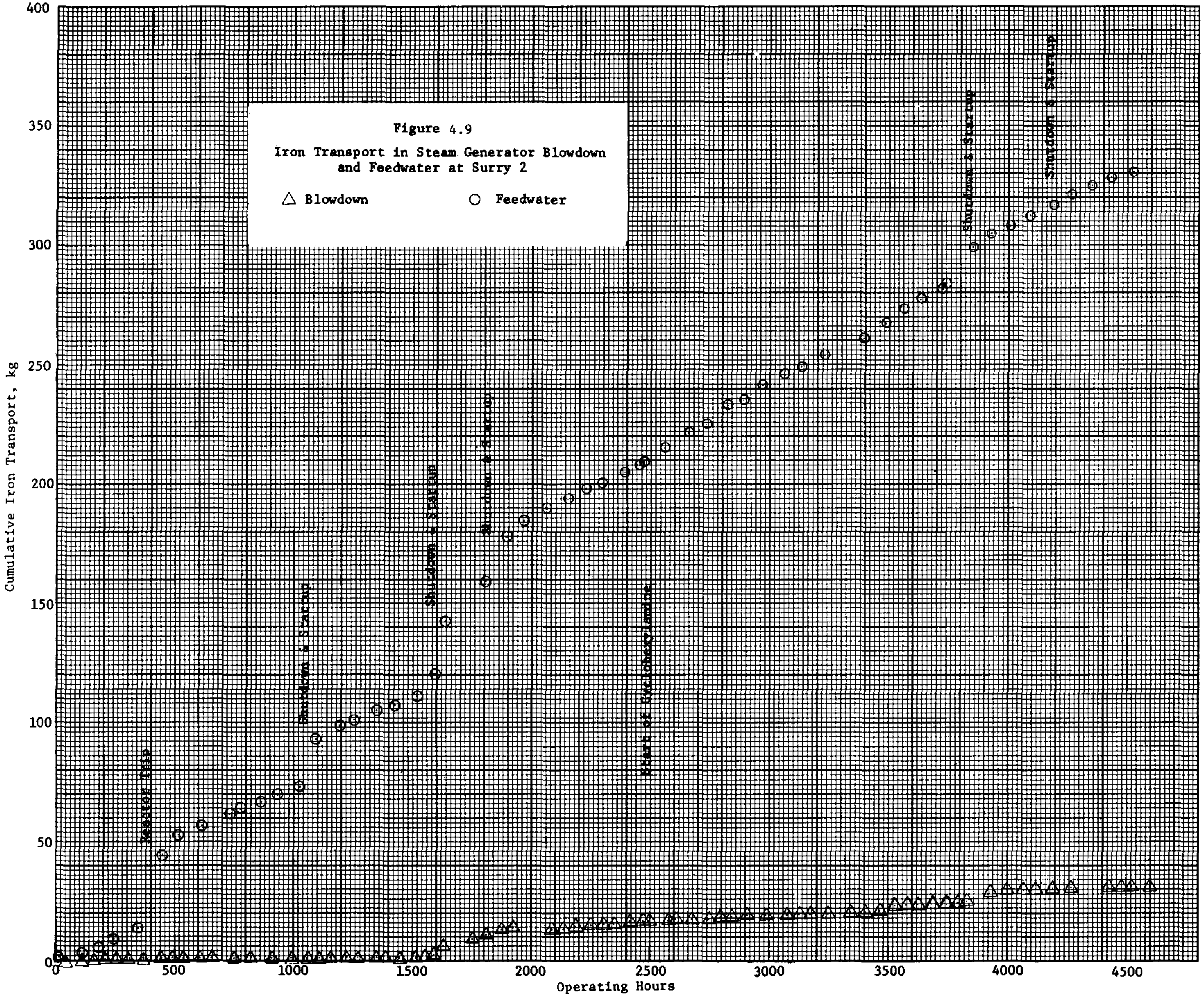


Figure 4.9

Iron Transport in Steam Generator Blowdown and Feedwater at Surry 2

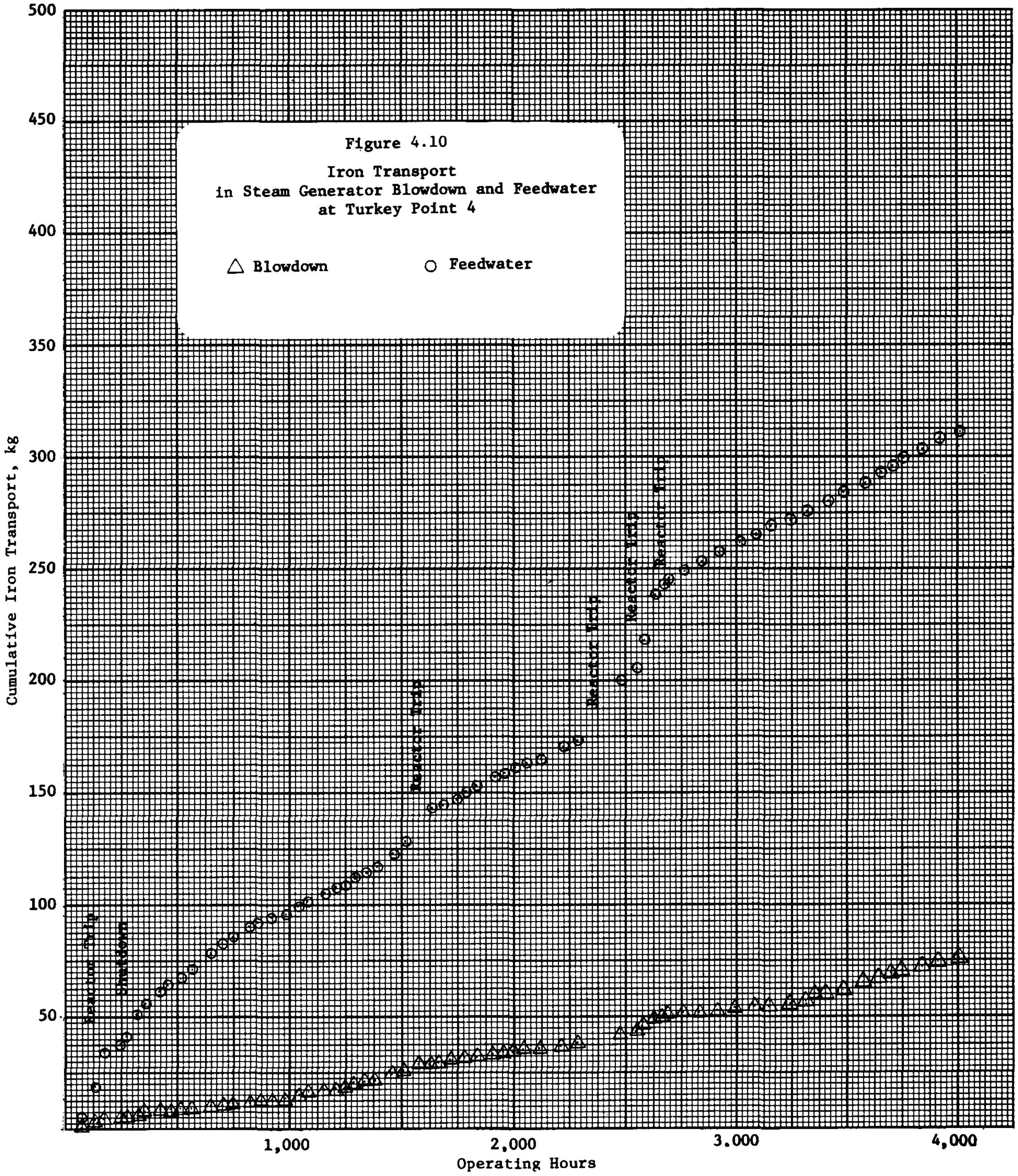


Figure 4.10

Iron Transport in Steam Generator Blowdown and Feedwater at Turkey Point 4

TABLE 4.3

STEAM GENERATOR BLOWDOWN AND FEEDWATER CORROSION PRODUCT TRANSPORT RATES

Station		Feedwater grams/h (sampling hours)	Blowdown grams/h (sampling hours)	Blowdown Efficiency %
Calvert Cliffs 1	Iron	134 (1120)	8 (1080)	6
	Copper	5.8	0.2	3
	Nickel	5.8	0.2	3
Prairie Island 1	Iron	47 (2500)	12 (2500)	25
	Copper	NA	NA	NA
	Nickel	0.7 (230)	0.2 (185)	30
Prairie Island 2	Iron	61 (3000)	21 (2800)	34
	Copper	NA	NA	NA
	Nickel	1.0 (1390)	0.2 (1380)	23
Surry 2	Iron	73 (4500)	6.8 (4600)	9
	Copper	15	1.0	7
	Nickel	2.7 (2560)	0.4 (2680)	16
Turkey Point 4	Iron	78 (4000)	19 (4000)	25
	Copper	11	0.7	6
	Nickel	9.0 (2760)	1.3 (2760)	14

NA - Not applicable

TABLE 4.4

POWER NORMALIZED FEEDWATER AND STEAM GENERATOR BLOWDOWN CORROSION PRODUCT TRANSPORT RATES

Station		Feedwater grams/h-MWe	Blowdown (sampling hours)	Blowdown Efficiency %
Calvert Cliffs 1	Iron	1.59 E-1 (1120)	9.74 E-3 (1080)	6
	Copper	6.84 E-3	2.14 E-4	3
	Nickel	6.92 E-3	2.26 E-4	3
Prairie Island 1	Iron	8.91 E-2 (2500)	2.24 E-2 (2500)	25
	Copper	NA	NA	NA
	Nickel	1.30 E-3 (230)	3.96 E-4 (185)	30
Prairie Island 2	Iron	1.15 E-1 (3000)	3.91 E-2 (2800)	34
	Copper	NA	NA	NA
	Nickel	1.83 E-3 (1390)	4.15 E-4 (1380)	23
Surry 2	Iron	9.27 E-2 (4500)	8.57 E-3 (4600)	9
	Copper	1.85 E-2	1.28 E-3	7
	Nickel	3.45 E-3 (2560)	5.58 E-4 (2680)	16
Turkey Point 4	Iron	1.12 E-1 (4000)	2.75 E-2 (4000)	25
	Copper	1.55 E-2	9.67 E-4	6
	Nickel	1.30 E-2 (2760)	1.80 E-3 (2760)	14

NA - Not Applicable

from the steam generator varying between approximately 5 and 35%. Somewhat lower efficiencies for the removal of copper from the steam generator were observed.

The implications of the steam generator mass balance data are twofold. First, utilization of a steam generator blowdown of 0.1 to 0.3% of the feedwater flow as a means to remove corrosion products during normal operation from the steam generator is not effective. Unfortunately, because of limitations of the plants in the study, it was not possible to significantly increase blowdown percentage to determine if this would result in increased removal rates of corrosion products.

Second, transport of iron via the feedwater at all ferrous plants such as Prairie Island 1 and 2 can be maintained at approximately the same level as that occurring at plants containing copper alloys although the carbon steel area at Prairie Island 1 and 2 is approximately 3 times that at plants with copper alloys. The ability of Prairie Island to operate with minimal feedwater iron transport rates results from the absence of the copper alloys in the system which allows operation at a feedwater pH of 9.4 to 9.6. At other plants in the study, feedwater pH generally is 0.3 to 0.5 units lower and cannot be significantly increased without raising questions concerning the increased corrosion rates of copper bearing alloys.

It should be recognized that transients, such as startups, shutdowns, power reductions or escalations, etc., lead to significant increases in the rate of corrosion product transport throughout the secondary cycle. Without including effects of such transients, significantly lower mass transport rates would have been estimated. Reference to Figures 4.7 to 4.10 clearly shows the effects of transients. For example, in Figure 4.10, reactor trips lead to significant increases in mass transport on several occasions. Provision for cleanup in the condensate cycle prior to power escalation following a trip would be expected to reduce corrosion product transport rates. However, it appears that corrosion product transport rate increases also occur during the thermal transient associated with initiating steam flow to the heaters, reheaters, etc. Thus, even if a system were provided with full flow condensate treatment, provision would have to be made to cascade all drains to the hotwell during startup periods to minimize such input.

Mass Transport Evaluation: Feedwater System

The second general area where the corrosion product transport data were employed was in the evaluation of sources of feedwater corrosion products, i.e., what fraction of the corrosion products resulted from corrosion of feedwater heater materials, condenser materials, reheaters, etc. Results of this evaluation are summarized in Table 4.5. Iron transport rate curves are shown in Figures 4.11 through 4.15. With reference to Table 4.5, it can be seen that from 67 to 85% of the total feedwater iron corrosion product burden was a result of corrosion in the condenser and low temperature extraction lines, heater shells, etc. As such, full flow condensate treatment using either deep bed demineralizers or powdered resin filter demineralizers could be employed to significantly reduce the total input of corrosion products to the steam generator and in all probability the buildup of sludge. As previously noted, the higher transport rate of iron in the feedwater and condensate at Calvert Cliffs could have resulted from their operation at a lower pH than the other monitored plants (see Figures 3.1 to 3.5). The condensate demineralizers were bypassed during most of the period covered by the transport data.

Copper transport was shown to follow a similar pattern at the three plants of pertinence with the condensate transport accounting for 52 to 86% of the total feedwater burden. Again, the implication is that installation of full flow condensate treatment would significantly reduce the buildup of copper bearing sludge in the steam generators. At all plants except Calvert Cliffs, 10 to 40% of the nickel transported via the feedwater resulted from corrosion of the low temperature materials in the cycle. The higher transport rate in the condensate at Calvert Cliffs probably results from the 70/30 copper nickel

TABLE 4.5

FEEDWATER AND CONDENSATE CORROSION PRODUCT TRANSPORT

Station		Feedwater grams/h (sampling hours)	Condensate grams/h (sampling hours)	Condensate/Feedwater %
Calvert Cliffs 1	Iron	120 (1310)	88 (1310)	74
	Copper	5.1	4.1	80
	Nickel	5.2	4.7	89
Prairie Island 1	Iron	48 (2400)	34 (2400)	69
	Copper	NA	NA	NA
	Nickel	0.7 (230)	0.2 (230)	25
Prairie Island 2	Iron	69 (2600)	59 (2500)	85
	Copper	NA	NA	NA
	Nickel	1.0	0.25	25
Surry 2	Iron	84 (2400)	56 (2400)	67
	Copper	14.7	7.7	52
	Nickel	1.9	0.7	37
Turkey Point 4	Iron	85 (4500)	64 (4500)	71
	Copper	11.8	10.2	86
	Nickel	9.0	1.0	11

NA - Not Applicable

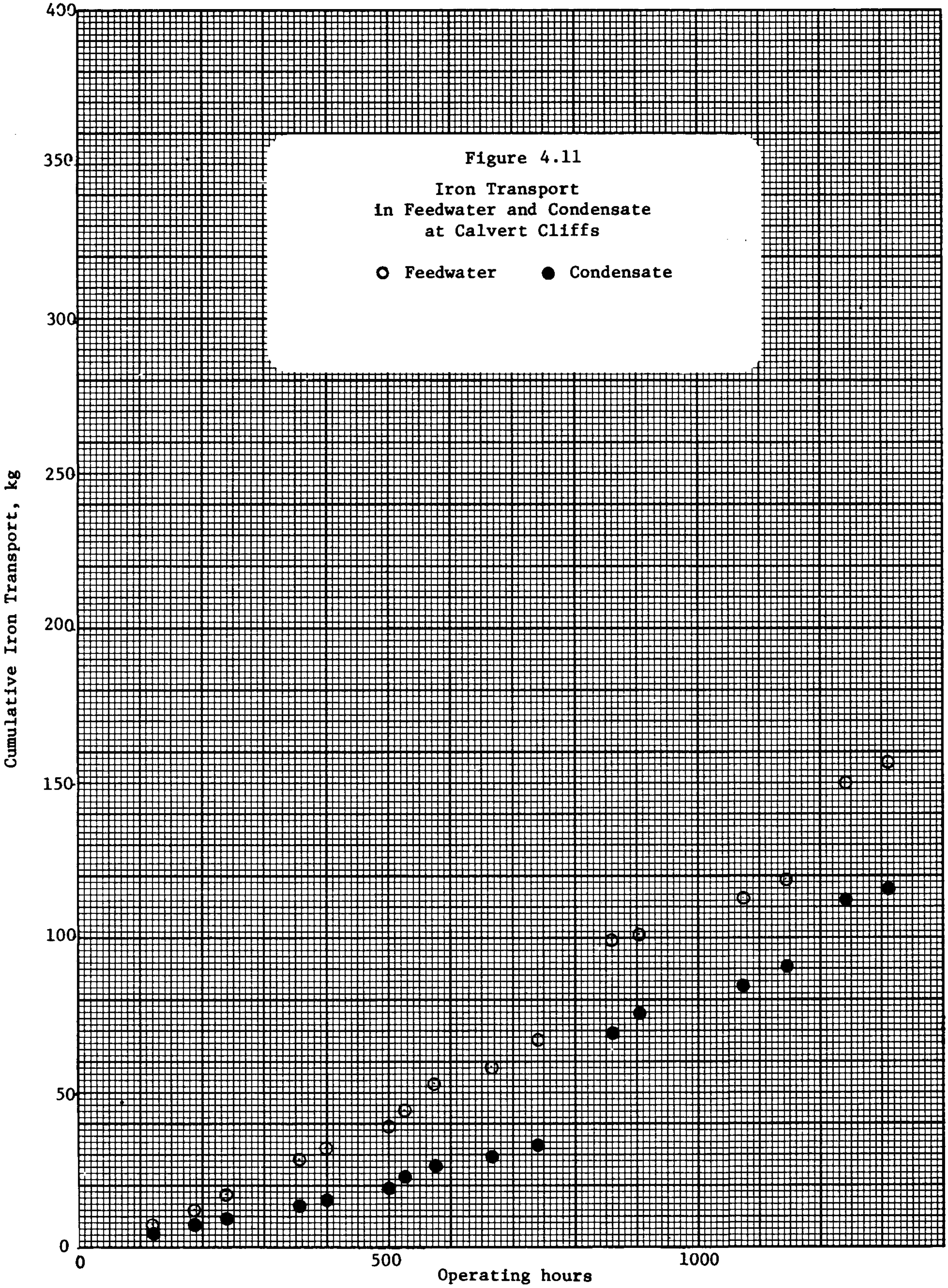


Figure 4.11

Iron Transport in Feedwater and Condensate at Calvert Cliffs

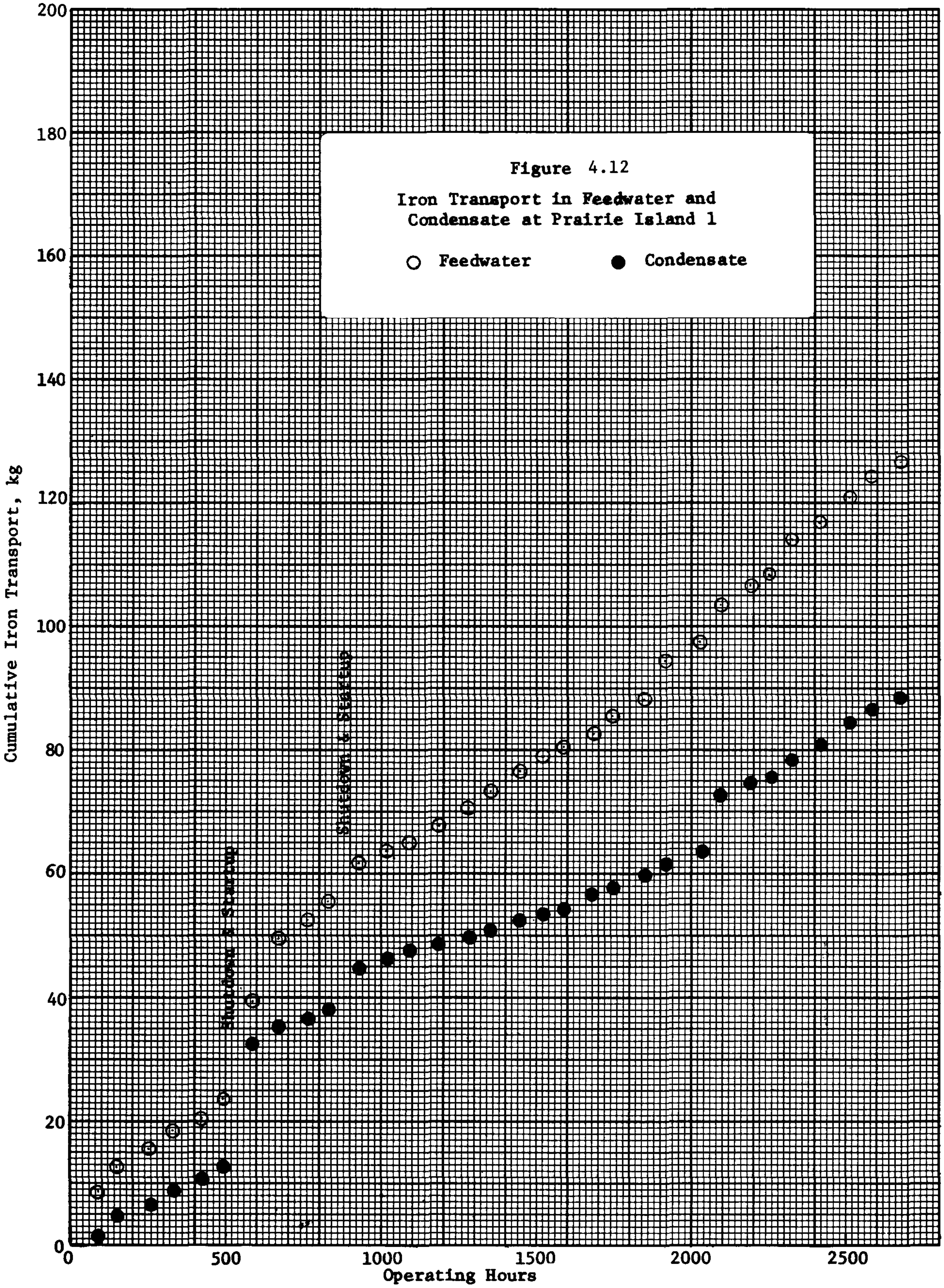


Figure 4.12

Iron Transport in Feedwater and Condensate at Prairie Island 1

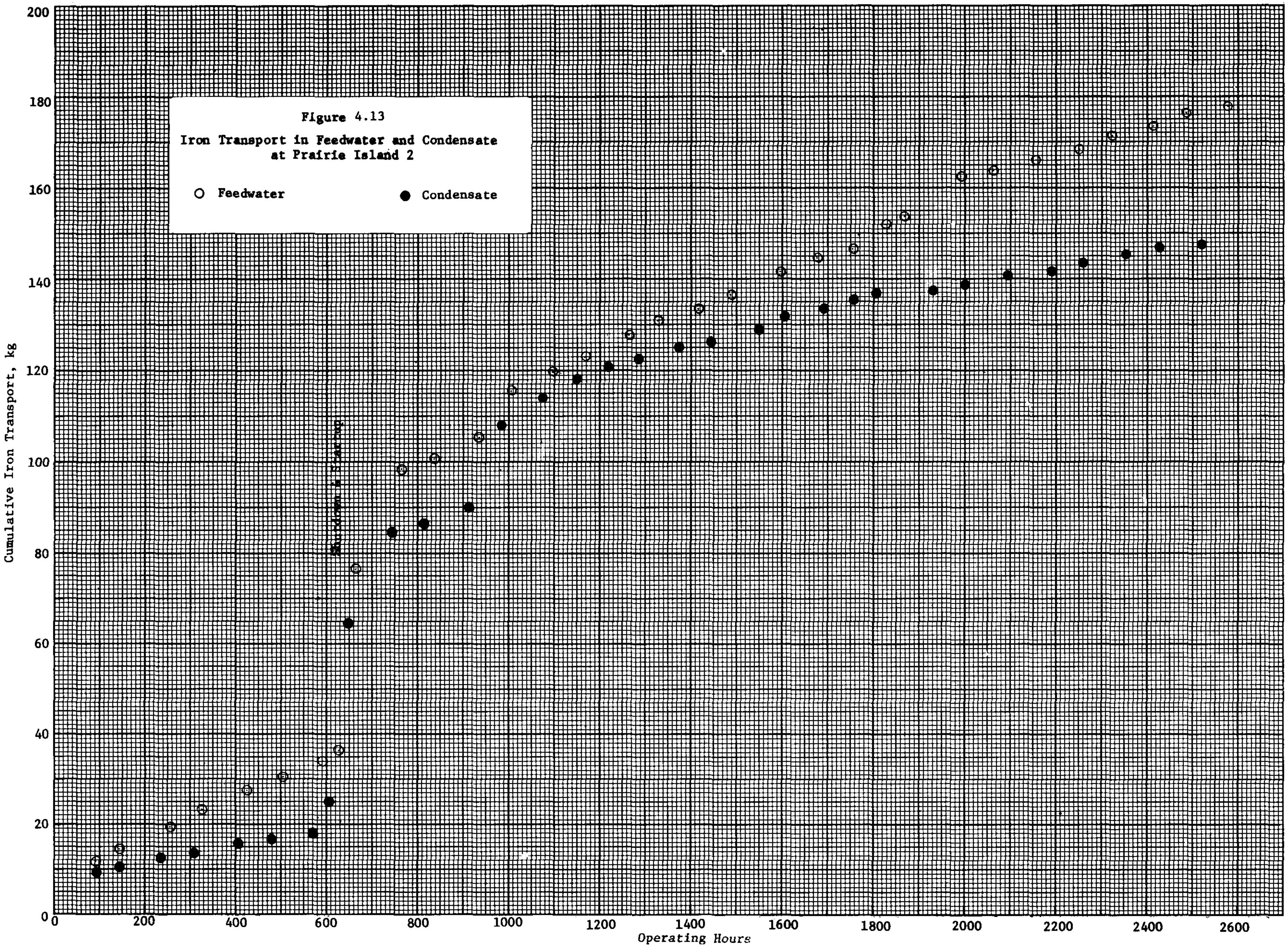


Figure 4.13

Iron Transport in Feedwater and Condensate at Prairie Island 2

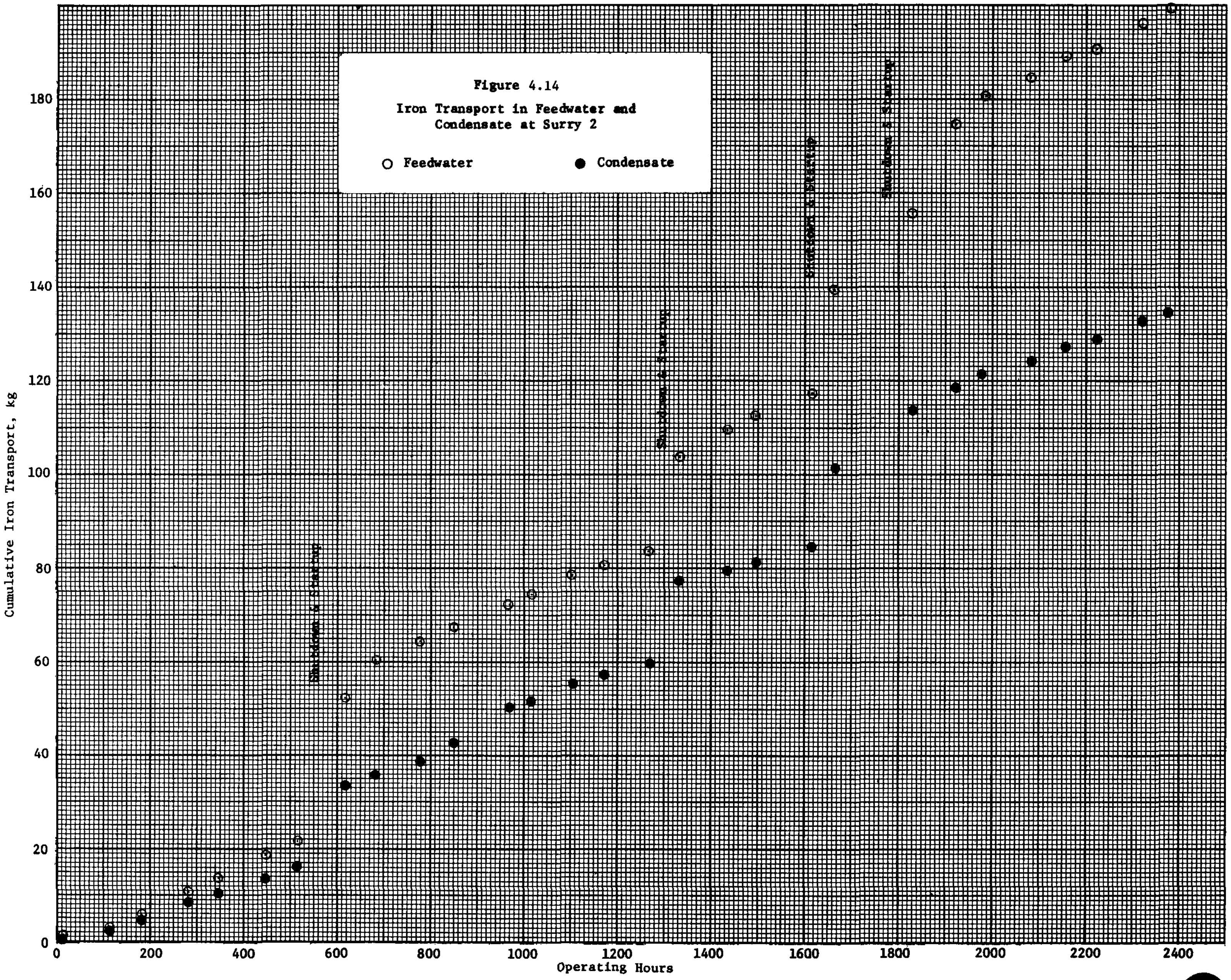


Figure 4.14

Iron Transport in Feedwater and Condensate at Surry 2

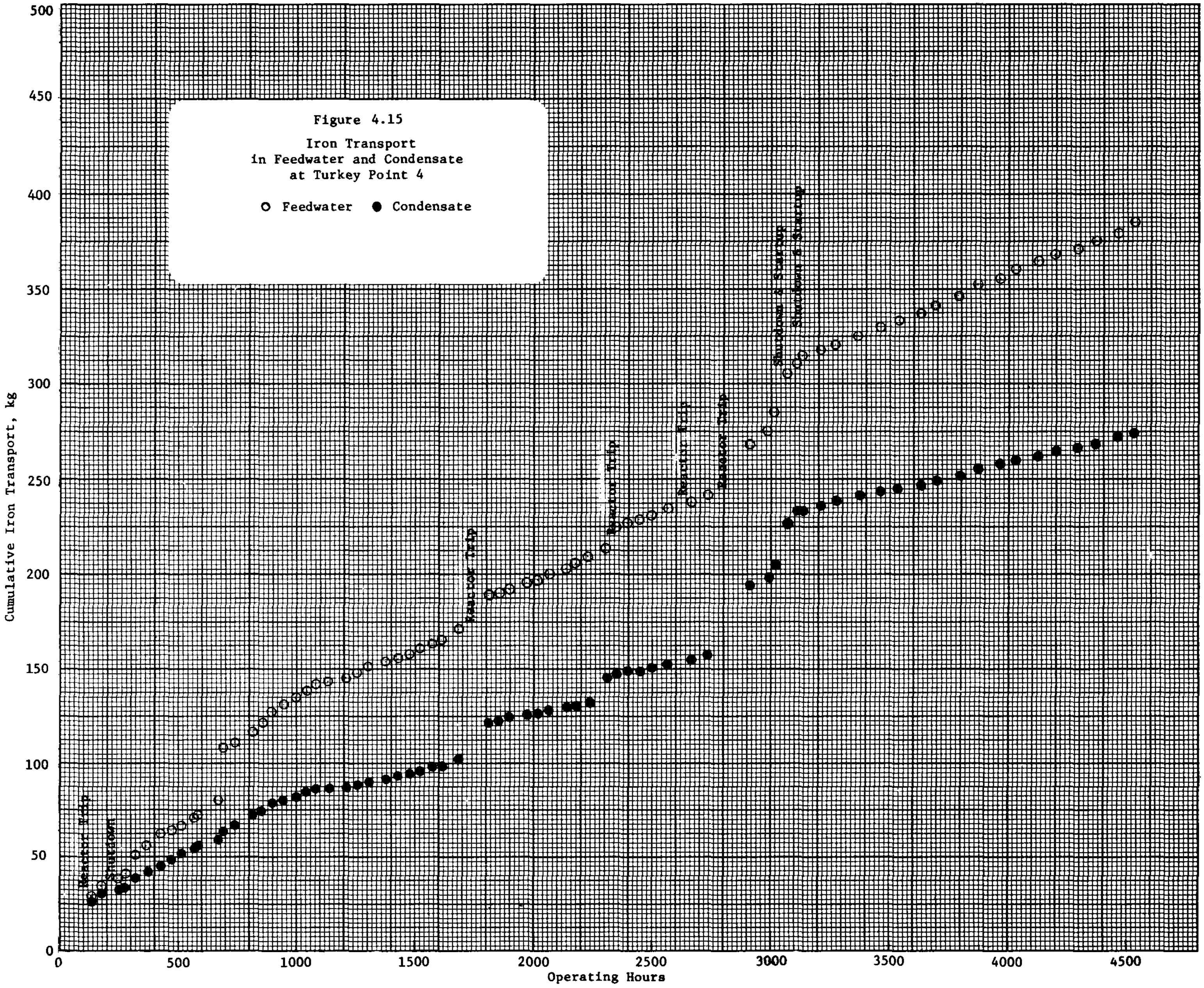


Figure 4.15

Iron Transport in Feedwater and Condensate at Turkey Point 4 tubed condenser. As previously noted, the relatively high nickel transport rate in the feedwater at Turkey Point 4 as compared to the other plants probably results from the Monel tubed high pressure feedwater heater.

In November 1975, Surry 2 changed from ammonia to cyclohexylamine pH control in the secondary system. Comparison of feedwater corrosion product transport rates subsequent to this change shows that iron transport rates were not significantly impacted by the transition (Figure 4.9). However, the copper transport rate via the feedwater subsequent to the transition increased by a factor of 2 as shown in Figure 4.16. Such an increase would be expected in that a higher feedwater system pH resulted with cyclohexylamine because of its larger steam to water phase distribution coefficient at high temperature. In particular, in the absence of significant amounts of unbalanced anionic impurities such as carbon dioxide, maintaining blowdown pH at 9 with ammonia would lead to a feedwater pH of approximately 9.3 whereas with cyclohexylamine, feedwater pH would be nearer to 10. An increase of approximately 0.5 units in feedwater pH was noted at Surry 2 subsequent to the transition. However, a portion of this change may have resulted from differences in primary to secondary leak rate, unbalanced anionic impurities from air inleakage, etc., prior and subsequent to the transition. Concurrent with the copper transport rate increase, it would have been expected that a decrease in iron transport would have resulted with the feedwater pH increase. That this was not observed may be a result of differences in the steam to water distribution coefficient of ammonia and cyclohexylamine and its effect on drain side corrosion rates.

At Prairie Island 2 and Surry 2, relatively extensive sampling programs also were carried out to relate corrosion product transport in the high pressure heater drains (HPD) to that in the feedwater (Table 4.6). At both plants, iron transport via the HPD was 15 to 30% of the total feedwater transport while nickel transport was 20 to 25% of the feedwater transport. Copper HPD transport at Surry was equivalent to approximately 30% of the feedwater burden. Copper and iron concentrations in the HPD were comparable to those in the condensate at both plants. Samples also

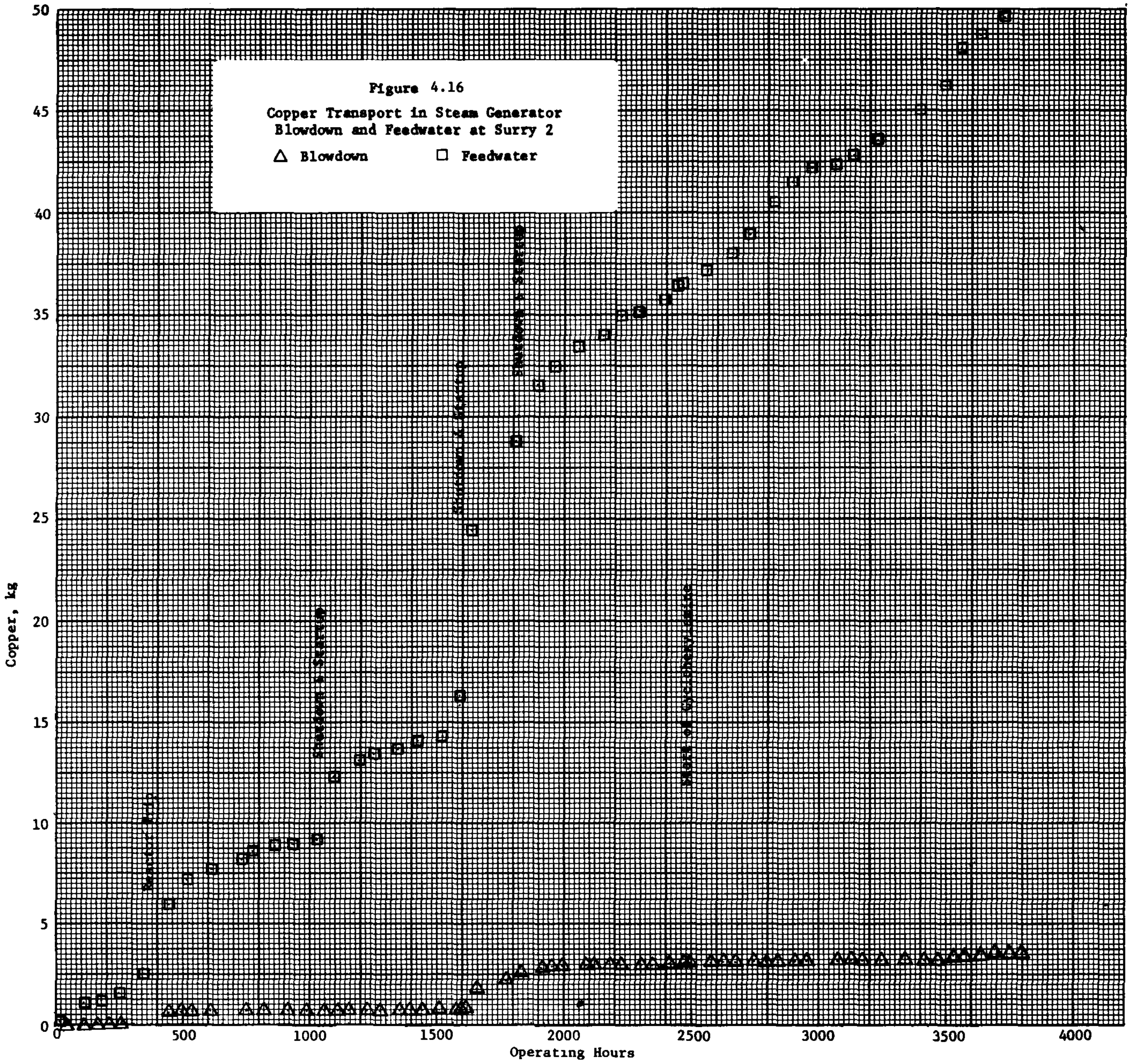


Figure 4.16

Copper Transport in Steam Generator Blowdown and Feedwater at Surry 2

TABLE 4.6

FEEDWATER, HIGH PRESSURE DRAIN AND MOISTURE SEPARATOR DRAIN CORROSION PRODUCT TRANSPORT RATES

grams/h (sampling hours)

Station		Feedwater	High Pressure Drain	Moisture Separator Drain
Calvert Cliffs 1	Iron	119.5 (1310)	NA	NA
	Copper	5.1	NA	NA
	Nickel	5.2	NA	NA
Prairie Island 1	Iron	47.2 (2490)	NA	NA
	Copper	NA	NA	NA
	Nickel	0.7 (230)	NA	NA
Prairie Island 2	Iron	40 (2980)	6.8 (2970)	5.8 (2950)
	Copper	NA	NA	NA
	Nickel	1.01	0.2	0.1
Surry 2	Iron	59.8 (4470)	19.1 (4480)	NA
	Copper	17.5	4.8	NA
	Nickel	3.5	1.2	NA
Turkey Point 4	Iron	85.0 (4530)	NA	NA
	Copper	11.8	NA	NA
	Nickel	9.0 (3060)	NA	NA

NA - Not available

were obtained from the moisture separator drains at Prairie Island 2. In the all ferrous Prairie Island 2 system, iron transport in the moisture separator drain constituted approximately 80% of iron transport in the HPD thus indicating that the primary source of iron in the pumped forward drains at Prairie Island results from corrosion of crossover piping or moisture separator internals and not from corrosion of drain piping, high pressure extraction piping,high pressure feedwater heater shells, or reheater tubing.

Hardness Element Transport

During the corrosion product transport study, concentration and transport data throughout the secondary system also were obtained for calcium and magnesium. These data are summarized in Table 4.7. As indicated, less than 10% of the calcium and magnesium input to the steam generators via the feedwater was removed via blowdown. Transport of calcium and magnesium throughout the secondary system in several of the plants suggests steam solubility of both species at the sub ppb level. This observation in based on the presence of calcium and magnesium in the high pressure drains and moisture separator drains at Prairie Island 2 and Surry 2. It is not currently possible to explain such observations on the basis of sampling and/or analytical errors.

TABLE 4.7

CONDENSATE, FEEDWATER, STEAM GENERATOR BLOWDOWN, HIGH PRESSURE DRAIN AND MOISTURE SEPARATOR DRAIN CALCIUM AND MAGNESIUM TRANSPORT RATES

grams/h (sampling hours)

Station		Condensate	Feedwater	Blowdown	High Pressure Drain	Moisture Separator Drain
Calvert Cliffs 1	Calcium	1.2 (1310)	1.9 (1310)	0.1 (1080)	NA	NA
	Magnesium	0.8	1.2	0.02	NA	NA
Prairie Island 1	Calcium	NA	NA	NA	NA	NA
	Magnesium	NA	NA	NA	NA	NA
Prairie Island 2	Calcium	0.6 (2540)	0.8 (2810)	0.1 (1380)	0.3 (2810)	0.08 (2790)
	Magnesium	0.3 (2800)	0.4	0.04	0.10	0.03
Surry 2	Calcium	0.4 (390)	2.0 (4470)	0.06 (2680)	0.6 (4480)	NA
	Magnesium	1.9	3.6	0.1	1.2	NA
Turkey Point 4	Calcium	1.6 (3060)	2.4 (3060)	0.1 (2760)	NA	NA
	Magnesium	1.3	1.6	0.05	NA	NA

Section 5

STEAM GENERATOR CHEMISTRY DURING LAYUP-STARTUP-STANDBY CONDITIONS

Layup chemistry practices differ somewhat from plant to plant. At Prairie Island 1 and 2, attempts are made to maintain a hydrazine concentration above 150 ppm with a pH above 10. A similar practice is pursued at Calvert Cliffs with liquid recirculated from generator to generator to promote initial hydrazine equilibration. At Surry, generators were isolated with no chemical additions at shutdown during most of the program. Later in the program hydrazine was employed on several occasions. Periods of dry layup up to one week also have occurred. At Turkey Point 4, layup procedures also have varied over the course of the program. Although, hydrazine and ammonia are generally added during extended shutdowns, units are sometimes put in dry layup for periods up to a week during inspections or maintenance.

Representative steam generator coolant samples generally are not available during periods of layup in that blowdown is terminated with shutdown. As such, the analyses of such samples are suspect with respect to representing the average bulk coolant chemistry in the generator during layup. For this reason, quantitative consideration of the chemistry of the samples obtained during layup was not possible. However, attempts were made to evaluate trends in steam generator chemistry noted during startup and shutdown transients when blowdown was being employed. Emphasis was placed on qualitatively assessing the hideout or precipitation of species which occurred during normal operation as manifested by their return during shutdown, cooldown, or startup periods.

At Prairie Island 2, a chemistry study was conducted during the startup of January 13 to January 21, 1976. After the unit commenced heatup for power operation, leakage developed on the reactor control rod drives, and a shutdown, cooldown, and depressurization ensued. Steam generator chemistry variations during this period and the subsequent startup are presented in Tables 5.1, 5.2, and 5.3. Calcium, magnesium, sodium, and chloride concentrations all were significantly greater than those observed

TABLE 5.1

PRAIRIE ISLAND STEAM GENERATOR 21 HEATUP AND COOLDOWN CHEMISTRY

JANUARY 13 to JANUARY 15, 1976

		Primary Temp. °C		Conductivity								
Date	Time		pH	Specific µmhos/cm	Cation µmhos/cm	Ammonia[a] ppm	Hydrazine[a] ppm	Sodium ppm	Sulfate ppm	Phosphate ppm	Chloride ppm	Silica ppm
1/13	1940	177	10.1	26.0	4.50	14	30	0.04	<1	<0.06	0.15	0.17
1/13	2105	204	10.1	23.5	4.30	16	38.8	0.045	<1	<0.06	0.30	0.20
1/13	2230	232	10.18	29.0	5.30	23	37.5	0.04	<1	<0.06	0.25	0.35
1/14	0100	260	10.30	36.0	5.40	45	22	0.08	<1	<0.06	0.30	0.55
1/14	0257	286	10.35	37.5	7.1	49	4.5	0.08	<1	<0.06	0.15	0.66
1/14	1515	243	9.90	21.8	6.4	6.5	0.37	0.035	<1	<0.06	0.30	0.28
1/14	1640	210	9.78	17.0	6.2	2.9	2.35	0.03	<1	<0.06	0.25	0.20
1/14	1730	182	9.72	15.8	6.8	2.6	2.40	0.035	<1	<0.06	0.30	0.18
1/14	1900	154	9.65	13.5	6.8	1.5	4.80	0.035	<1	<0.06	0.25	0.16
1/14	2035[b]	104	9.50	10.6	7.2	0.85	5.0	0.04	<1	<0.06	0.20	0.15
1/14	2400	94	10.28	47	6.2	33	160	0.04	<1	<0.06	0.20	0.13
1/15	0557	60	10.26	46	6.2	31	150	0.05	<1	<0.06	0.25	0.16

a) Measured one day after sampling
b) Started to add hydrazine for wet layup

TABLE 5.2

PRAIRIE ISLAND 2 HEATUP AND COOLDOWN CHEMISTRY

JANUARY 13 to JANUARY 15, 1976

(ppb)

			Steam Generator 21				Steam Generator 22			
Date	Time	Primary Temp. °C	Iron F	Nickel F	Calcium[b] NF	Magnesium[b] NF	Iron F	Nickel F	Calcium[b] NF	Magnesium[b] NF
1/13	1940	177	4230	23	180	8	342	28	390	30
1/13	2105	204	434	23	190	8	571	23	360	21
1/13	2230	232	211	14	170	8	178	16	350	15
1/14	0100	260	6270	32	130	3	294	20	260	8
1/14	0257	286	163	23	96	3	89	<15	180	4
1/14	1515	243	131	12	180	12	321	19	280	16
1/14	1640	210	230	20	190	26	1890	55	290	44
1/14	1730	182	271	17	250	34	1290	45	370	46
1/14	1900	154	111	12	270	51	712	32	320	51
1/14	2035[a]	104	117	13	280	51	607	29	230	46
1/14	2400	94	36	<9	140	18	151	19	170	25
1/15	0557	60	44	<11	110	18	151	21	85	21
		49	15	<10	170	24	18	15	100	25

a) Started to add hydrazine for wet layup
b) Filterable calcium and magnesium less than 8 and 13 ppb, respectively.

F: Filterable
NF: Nonfilterable

TABLE 5.3

PRAIRIE ISLAND 2 HEATUP CHEMISTRY

JANUARY 20 TO JANUARY 21, 1976

(ppb)

Steam Generator 21

Date	Time	Reactor Power %	Iron F	Nickel F	Copper F	Chrome F	Calcium F	Calcium NF	Magnesium F	Magnesium NF	Sodium F	Chloride F	Silica F
1/20	1645	5	9490	58	14	ND	11	290	17	10	183	140	2000
1/21	0845	62	10840	72	16	ND	ND	480	25	42	178	100	1500
1/21	1120	72	36740	249	51	16	ND	440	73	39	114	80	1400
1/21	1415	82	74750	569	114	39	17	470	128	52	108	70	1300

Steam Generator 22

Date	Time	Reactor Power %	Iron F	Nickel F	Copper F	Chrome F	Calcium F	Calcium NF	Magnesium F	Magnesium NF	Sodium F	Chloride F	Silica F
1/20	1645	5	14420	88	43	ND	ND	260	34	11	180	150	1700
1/21	0845	62	61440	800	162	56	19	400	87	34	110	70	1300
1/21	1120	72	72630	782	190	56	16	380	102	41	200	<50	1100
1/21	1415	82	94930	1015	211	81	13	360	129	47	92	<50	1100

F: Filterable

NF: Nonfilterable

ND: Nondetectable

during normal operation. As such, hideout of soluble species or precipitation of insoluble species during operation with subsequent return during transients is indicated.

During similar transients at Surry 2, significant buildups of sodium, chloride, phosphate, etc., occur in the generators as evidenced by their high concentrations in the blowdown prior to plant startup. In February 1976, data were gathered immediately preceding and during the cooldown of Unit 2 for primary to secondary leakage. Increasing concentrations of calcium, magnesium, chloride, phosphate and sulfate were observed in the blowdown as the unit was cooled from 232 to 66°C (Table 5.4). The hardness element increases are probably attributable to the increase in solubility of such species as magnesium hydroxide, calcium hydroxide, and calcium sulfate with decreasing temperature. Precipitation of such species is predicted to occur in the event of cooling water ingress at a seawater cooled plant by the modeling studies discussed in Section VII of this report.

An additional opportunity to obtain transient chemistry data became available in July 1976 during a Surry 2 shutdown. Results of the monitoring program performed during this period are summarized in Table 5.5. Although the cooldown-heatup chemistry differed widely between generators, the return of species not generally observed in the steam generator during normal operation was again evident. The results at Surry clearly demonstrate that the phenomenon known as hideout or precipitation of hardness elements in different forms with subsequent return is an item requiring detailed consideration in future evaluations.

Following a primary to secondary leak in generator 4C at Turkey Point 4 on September 9, the unit was shut down. After cooldown, generator 4A was placed in wet layup; generators 4B and 4C were left at normal operating levels in preparation for a tube leakage inspection. Following generator tube repairs, generators 4B and 4C were drained for maintenance. In preparation for startup, levels in all three generators were adjusted to

TABLE 5.4

SURRY 2 COOLDOWN STEAM GENERATOR CHEMISTRY

FEBRUARY 3, 1976

(ppb)

Steam Generator	Time	Temp. °C	Iron		Nickel		Copper		Calcium		Magnesium		Sodium	Chloride	Sulfate	Silica	Phosphate	Blowdown m^3/h
			F	NF	F	NF	F	NF	F	NF	F	NF	NF	NF	NF	NF	NF	
A	1000	286	<16	<70	<16	<70	<12	<40	<20	<40	<8	30	90	60	<100	35	<10	11.3
	1650	232	7.6	<70	<6	<70	3.8	<40	<4	<40	<3	120	1400	1000	1000	130	110	
	1900	177	75.5	<70	9.4	<70	9.4	70	9.4	<40	<4	280	1400	1200	800	170	540	
	2115	121	7.9	<70	<8	<70	0	<40	9.2	<40	<4	420	1500	600	1000	120	700	
	2375	66	100	<70	8.5	<70	0	<40	10.6	70	11.7	600	1600	1400	1100	130	1200	
B	1000	286	<16	<70	<16	<70	<12	<40	<18	<40	<8	50	160	180	<100	75	<10	11.3
	1650	232	<12	<70	<12	<70	<8	<40	<14	<40	<6	100	1700	2300	400	210	60	
	1900	177	800	<70	53	<70	13.5	100	<8	<40	3.1	240	1900	1800	900	200	530	
	2115	121	153	<70	<15	<70	7.1	<40	<17	<40	<8	540	2400	2000	700	190	800	
	2375	66	64.5	<70	6.6	<70	<8	<40	28.2	60	12.1	710	2200	2200	1200	200	1300	
C	1000	286	<17	<70	<17	<70	<12	<40	<24	110	<13	75	310	370	<100	90	<20	11.3
	1650	232	5.3	<70	<7	<70	<5	<40	<8	<40	<4	100	1700	1800	100	260	180	
	1900	177	1757		109		40.5		<20	<40	<9	430	2000	2000	500	230	400	
	2115	121	130		<16		<10		<18	<40	<8	730	1800	1900	600	200	800	
	2375	66	138		<15		<10		<18	<40	12.2	1390	2500	2300	700	270	1700	

F: Filterable

NF: Nonfilterable

TABLE 5.5

SURRY 2 STEAM GENERATOR COOLDOWN-HEATUP CHEMISTRY

JULY 30 TO JULY 31, 1976

Date	Time	Temp. °C	Cyclohexylamine ppm	Ammonia ppm	Hydrazine ppm	Cation Conductivity	Calcium ppm	Magnesium ppm	Sodium ppm	Chloride ppm	Silica ppm	Phosphate ppm	Blowdown m^3/h
Steam Generator A													
7/30	1345	204	4.4	0.27	<0.01		<0.03	0.199	2.1	3.5	0.085	0.28	1.1
7/31	1840	224	3.8	0.13	<0.01		0.097	0.683	4.9	8.9	0.099	0.26	0
	1935	249	3.3	0.14	<0.01		0.097	0.696	5.0	9.4	0.110	0.28	0
	2040	271	2.5	0.11	<0.01		0.065	0.364	6.0	10.7	0.123	0.24	0
	2145	286	2.1	0.10	<0.01		0.087	0.281	6.8	12.0	0.129	0.24	0
Steam Generator B													
7/30	1345	204	3.9	0.40	<0.01		<0.03	0.171	2.2	3.6	0.085	0.30	1.1
	1505	177	5.7	0.26	<0.01		<0.03	0.039	2.3	3.8	0.098	0.39	1.1
7/31	1045	177	6.2	0.31	<0.01		NM	NM	3.1	5.8	0.100	0.53	0
	1840	224	6.6	0.28	<0.01		<0.03	0.266	3.2	5.5	0.079	0.39	0
	1935	249	6.0	0.28	<0.01		<0.03	0.217	3.3	5.8	0.088	0.39	0
	2040	271	5.8	0.28	<0.01		<0.03	0.141	3.5	5.8	0.100	0.32	0
	2145	286	6.0	0.26	<0.01		<0.03	0.094	3.3	6.0	0.110	0.26	0
Steam Generator C													
7/30	1345	204	7.5	0.22	<0.01	NM	<0.03	0.173	0.68	1.2	0.083	0.29	1.1
	1505	177	4.6	0.30	<0.01	NM	<0.03	0.223	0.74	1.1	0.099	0.37	1.1
7/31	1045	177	4.4	0.23	<0.01	45.4	NM	NM	2.4	3.8	0.110	0.56	0
	1840	224	4.4	0.17	<0.01	58.5	<0.03	0.204	3.0	4.0	0.090	0.64	0
	1935	249	3.9	0.16	<0.01	61.6	<0.03	0.162	3.1	4.1	0.101	0.69	0
	2040	271	3.3	0.16	<0.01	63.6	<0.03	0.089	3.3	4.5	0.101	0.61	0
	2145	286	3.6	0.17	<0.01	60.0	<0.03	0.048	3.3	4.5	0.123	0.60	0

* NM: Not measured

All values measured at 35 ± 1°C

the normal operating range. After normal level was achieved, the chemistry indicated in Table 5.6 was observed. Significant concentrations of seawater impurities were present in steam generator 4A which was not drained and refilled during the maintenance outage.

Only limited data are available for Calvert Cliffs 1. However, return of condenser cooling water species is indicated with reactor power transients. For example, sodium concentration subsequent to a reactor trip on September 29, 1976 increased to 0.1 ppm from a normal level prior to this transient on the order of 10 ppb. Unfortunately, concurrent chloride concentration analyses were not performed.

On the basis of the chemistry observations made during periods of plant shutdowns or restarts, it is evident that hideout of soluble species as sodium chloride as well as precipitation of hardness compounds such as calcium hydroxide, magnesium hydroxide, or calcium sulfate occur to some extent at each of the 5 plants in the study as a result of condenser inleakage. The hideout phenomenon may be a result of boiling to dryness of steam generator bulk coolant in local areas of the generator where non-optimum thermal-hydraulics exist. Such areas could 1) encompass a number of tubes over a several foot length at a specific or varying location within the steam generator, 2) exist within sludge deposits, 3) exist within the tube to tube support plate interfaces, etc. In any event, the return of soluble species during cooldown after the steam bubbles are collapsed infers the presence of significant dryout regions within the generator.

As discussed in Section VII of this report, a preliminary model of solution chemistry during boiling has been developed to allow estimation of the cooling water chemistries in local areas where dryout is proceeding. At seawater, brackish water or cooling tower water sites, the formation of highly acidic solutions is expected to occur in such areas as dryout progresses. As such, acidic attack of materials such as carbon steel or Inconel would be expected. At a fresh water site, dryout is expected to

TABLE 5.6
TURKEY POINT 4
WET LAYUP CHEMISTRY

Steam Generator	4A	4B	4C
	September 14, 1976		
pH	10.02	8.99	9.68
Sodium, ppm	25.5	0.16	0.30
Chloride, ppm	43.3	0.5	0.10
Silica, ppm	0.94	0.27	0.40
Hydrazine, ppm	25.6	0.026	40.9
	September 28, 1976		
pH	9.22	9.76	9.28
Cation Conductivity, μmhos/cm	72.6	34.1	90.3
Sodium, ppm	1.1	0.35	0.83
Chloride, ppm	1.5	0.5	1.3
Silica, ppm	0.36	0.15	0.41
Hydrazine, ppm	63.6	29.7	40.7

lead to formation of significant concentrations of sodium hydroxide in such areas which could result in caustic stress corrosion cracking of Inconel. It is also possible that high concentrations of caustic could lead to aggressive corrosion of carbon steel components within the generator.

Section 6

EFFECTS OF CONDENSER LEAKAGE ON STEAM GENERATOR CHEMISTRY

Condenser leakage has been a recurring problem at each of the five study plants (Table 6.1). However, at the fresh water cooled sites, i.e., Prairie Island 1 and 2, low levels of condenser leakage on a continuous basis do not impact significantly on steam generator chemistry thereby allowing continued operation in the absence of any violation of secondary chemistry control parameters. At seawater and brackish water cooled sites, leakage of the same magnitude leads to chemistry transients in the steam generators requiring corrective action. At Surry 2 and Turkey Point 4, sawdust is employed to reduce condenser leakage temporarily prior to water box isolation, leak identification, and plugging. At Calvert Cliffs, full flow powdered resin filter demineralizers or partial flow deep bed demineralizers are placed in service on indication of leakage. In addition, steam generator blowdown at Calvert Cliffs can be increased to as high as 27 m^3/h (120 gpm) per generator which is significantly greater than the blowdown capabilities at the other units.

To determine the effects of condenser inleakage on steam generator chemistry at a fresh water site, Westinghouse performed a test program with simulated condenser leakage of 0.2 m^3/h at Prairie Island 2. The simulation was terminated after approximately 13 hours. Numerous blowdown samples were obtained. Plant instrumentation indicated only a small increase in steam generator pH from approximately 9.0 to 9.1. A significant increase in cation conductivity, from 1.2 to 2.8 and 1.6 to 4.1 μmhos/cm on steam generators 21 and 22, respectively, occurred during the injection. These levels are less than those expected if sulfate and chloride remained totally soluble in the steam generator coolant during injection. Such a deviation indicates that sulfate was precipitated in the steam generator possibly as calcium sulfate, or a hideout of soluble chloride or sulfate occurred in dryout regions. In any event, only minor system chemistry upsets were detected at a leakage magnitude which should be readily identifiable and repairable.

TABLE 6.1

CONDENSER TUBE PLUGGING HISTORY

	Calvert Cliffs	Prairie Island 1	Prairie Island 2	Surry 2	Turkey Point 4
Condenser Material	70/30 CuNi	Stainless	Stainless	90/10 CuNi	Al-Brass*
Cooling Water	Brackish	Fresh	Fresh	Brackish→Fresh	Seawater
Number of Tubes Plugged					
May - December 1973	NA	0	0	15	0
January - June 1974	NA	37	0	8	10
July - December 1974	NA	4	0	0	6
January - June 1975	22	0	0	0	4
July - December 1975	19	0	0	6	38
January - June 1976	1	0	0	265	46
July - December 1976	4	0	3	14	32

* Air removal section 70/30 CuNi; 1 of 4 water boxes retubed with titanium and 1 with 70/30 CuNi in May 1976.

At the brackish water cooled Surry 2 station and the seawater cooled Turkey Point 4 station, responses of steam generator chemistry to low level condenser leakage are more severe than those experienced at Prairie Island. In general, pH depressions occur with cooling water ingress as a result of magnesium hydroxide precipitation (see Section VII). With pH depression, the feedrate of volatile pH control additive is increased to return generator pH to the normal range. Several examples of the type of variations to be expected with seawater intrusion into a PWR on AVT are given below (more complete details are included in the seven progress reports[2-8]):

1. On March 24 to 25, 1976 at Turkey Point 4, a leak of approximately 0.6 to 2 liters/h was discovered. Generator acid conductivity increased to 30 to 50 μmhos/cm and chloride to 3 to 4 ppm. A pH decrease of 0.2 to 0.4 units occurred.[6]

2. On June 16, 1976 at Turkey Point 4, condensate chemistry at the inception of a leak showed chloride as high as 120 ppm. Chlorides in the blowdown were 400 ppm, cation conductivity near 1400 μmhos/cm with pH below 7.[7]

3. On March 10, 1976 at Calvert Cliffs 1, a leak of approximately 9 liters/h occurred. Steam generator chemistry showed sodium between 0.8 and 1 ppm, chloride between 1.7 and 1.9 ppm, and conductivity between 8 and 11 μmhos/cm. pH measurements were not recorded during this period.[6]

4. In August 1975, a leak of approximately 8 liters/h occurred at Surry 2. Even with blowdown increased from 3.4 m^3/h (15 gpm) to 9 m^3/h (40 gpm), sodium and chloride concentrations increased from <0.1 ppm to as high as 2.8 ppm and 5 ppm, respectively. Ammonia feedrate increases were necessary to maintain steam generator pH.[4]

Chloride concentrations in steam generator sludge are currently being related to the tube denting phenomenon being observed at several PWRs.

In view of this emphasis, a review of operating days above specific chloride levels was begun with the long term goal of relating tube damage to chloride exposure. Arbitrary blowdown chloride levels of >0.2, >1, >5, >10, and >20 ppm were chosen. Since chloride is not routinely measured at Calvert Cliffs while sodium is, chloride concentration was estimated from the chloride to sodium ratio in brackish water (1.54). This approximation could overestimate chloride exposure since condensate filters and demineralizers at Calvert Cliffs can input sodium to the generators in the absence of chloride.

Neither Westinghouse nor Combustion Engineering have a direct chloride specification. Westinghouse infers that chloride be maintained at <0.18 ppm (<2 μmhos/cm cation conductivity) during normal operation with operation at up to 10 ppm allowed for an unspecified number of periods each up to two weeks duration. A shutdown recommendation is inferred at chloride >10 ppm. The Combustion Engineering inferred chloride limit during normal operation is approximately 1.7 ppm (<7 μmhos/cm specific conductivity) at their midpoint recommended pH of 8.7.

Preliminary review results are given in Figures 6.1 to 6.3. The Calvert Cliffs data (Figure 6.1) from the January 1975 startup indicate difficulty in maintaining minimal sodium in the generators during 1975. Better control was indicated during 1976. Figure 6.2 for Surry 2 shows the total (phosphate followed by AVT) and the AVT only time of operation above designated chloride levels. Performance of the Surry 2 condenser relative to leakage has been poor since startup. Tighter chloride control, particularly at the higher chloride levels (1, 5, and 10 ppm), was maintained after changing to AVT (1975 and 1976) compared to operation with phosphates (1973 and 1974). Turkey Point 4 chloride exposure is shown in Figure 6.3 during phosphate followed by AVT operation and AVT only operation. The relative improvement in chloride control after changing to AVT chemistry is similar to that at Surry 2.

Surry 2 and Turkey Point 4 each experienced a steam generator tube failure during operation with phosphate chemistry. Several factors relative to

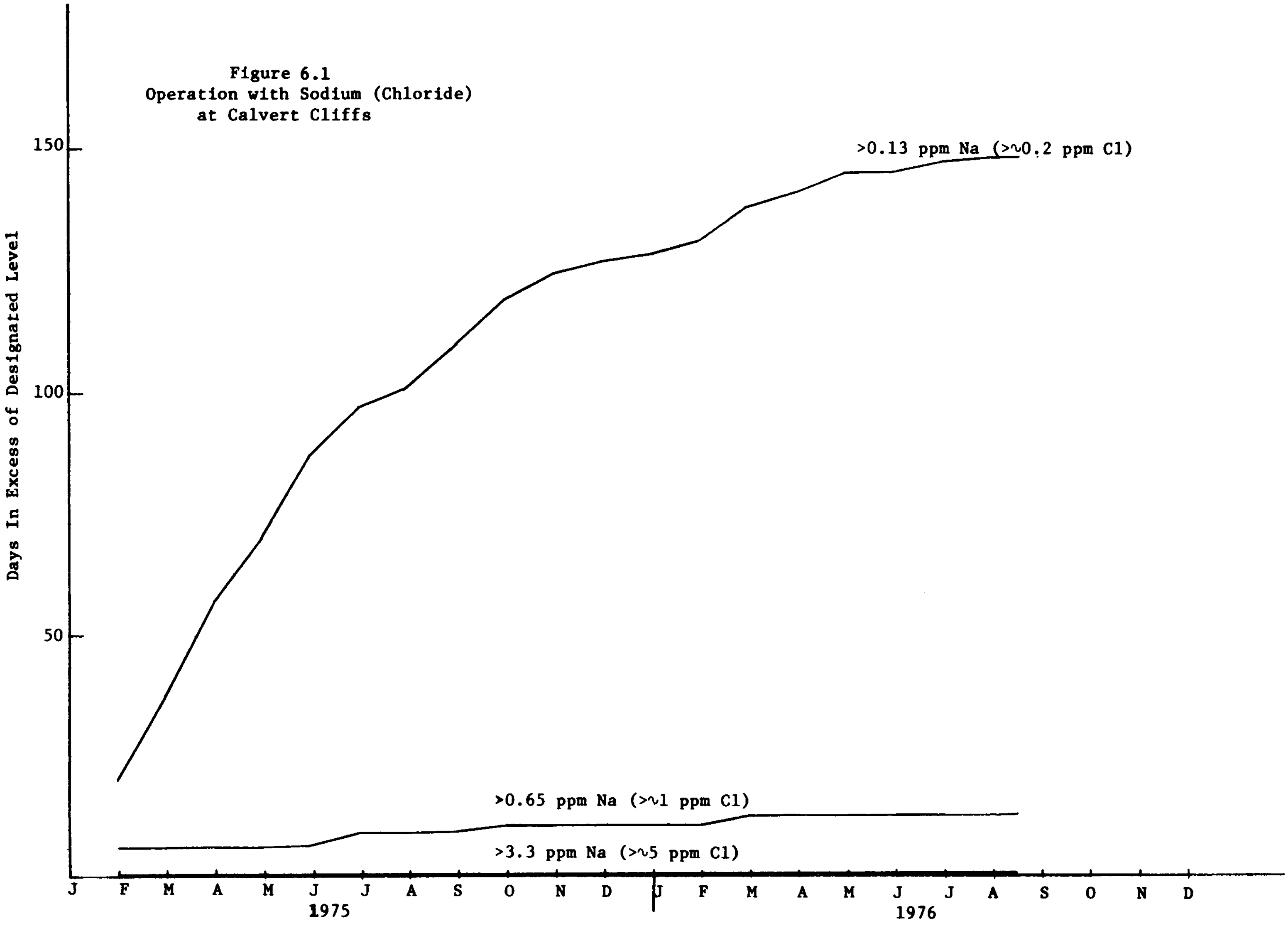


Figure 6.1
Operation with Sodium (Chloride)
at Calvert Cliffs

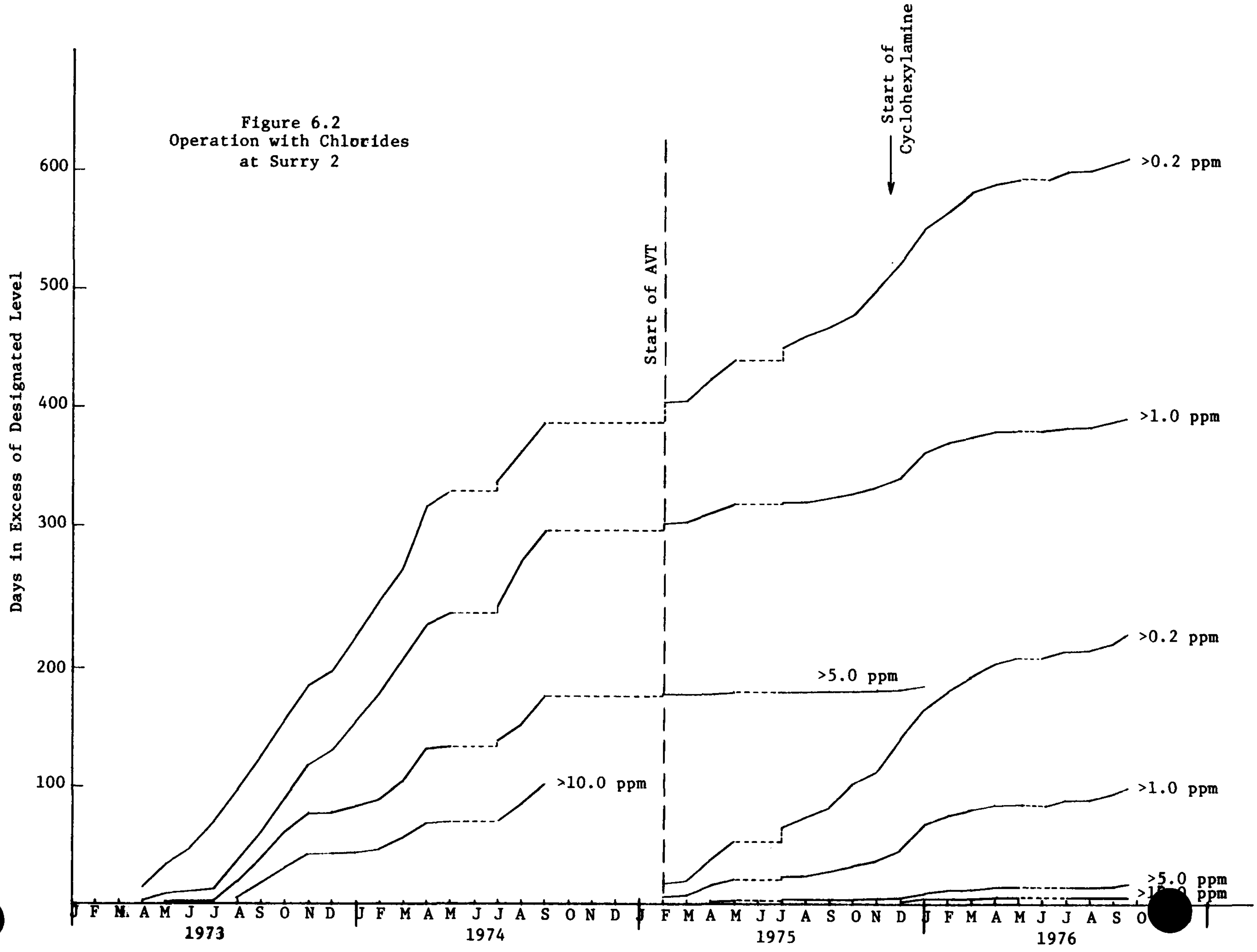


Figure 6.2
Operation with Chlorides
at Surry 2

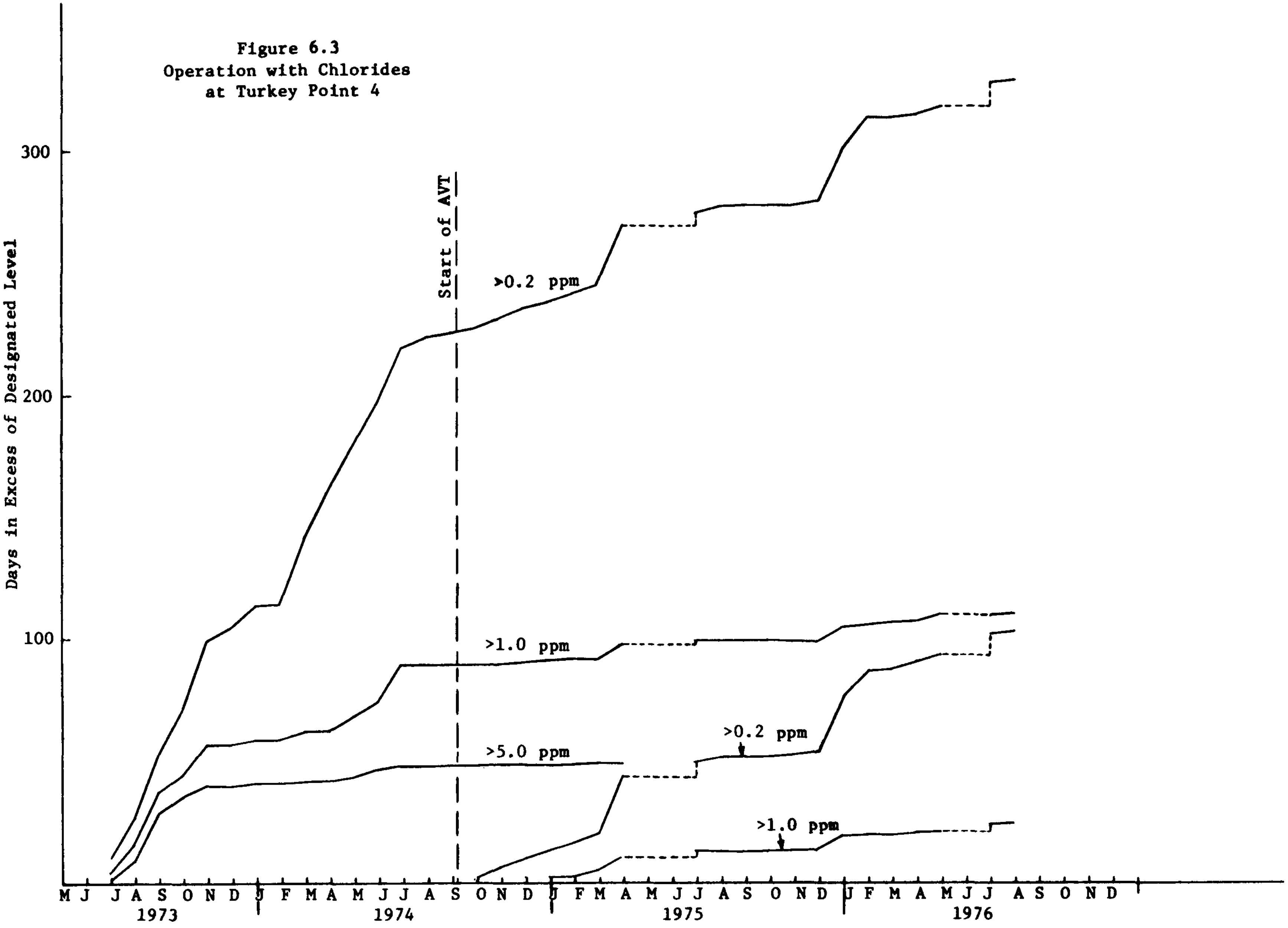


Figure 6.3
Operation with Chlorides
at Turkey Point 4

the first failure during phosphate chemistry and the first failure after change to AVT are compared in Table 6.2. Similar power operation in terms of effective full power years (EFPY) prior to the first tube failure is indicated although the chloride exposures differ significantly.

As an initial step in evaluating the effectiveness of condensate demineralization equipment to minimize effects of cooling water leakage on steam generator chemistry, several tests were performed on the condensate filter-demineralizer system at Calvert Cliffs 1. Six 1.52 m diameter vessels each containing 745 septums of 2.54 cm diameter and 1.31 m length provide for full flow condensate filtration using either a wood cellulose or powdered resin precoat. Each vessel contains 76 m^2 of filter area and is operated at 750 m^3/h at full load (9.9 m/h).

Chemistry transients at Calvert Cliffs in the feedwater and blowdown during a period of condenser leakage near the end of January 1976 are shown in Figure 6.4. The condenser had been leaking at a rate of $\sim$0.3 liters/h (0.0009 gpm) for about 32 hours before the insertion of the precoat filters. When filters were put in service at approximately 0920 on January 30, short duration changes occurred throughout the system (see Figure 6.5). Feedwater and steam generator cation conductivity showed peaks before decreasing with time. Blowdown pH and conductivity and steam conductivity decreased before returning to levels higher than those preceding the insertion. These changes suggest that significant air input to the secondary system occurred during filter insertion. This premise is supported by the observed oxygen increases in the feedwater. Excess hydrazine would be consumed by the oxygen resulting in pH and conductivity depressions before hydrazine or ammonia feedrates could be increased. Inputs of significant amounts of powdered resin also could explain these observations.

After the filters were removed from service at 0300 hours on January 31, condenser leakage was again indicated by an increase in cation conductivity. This leak of $\sim$1 liter/h (0.004 gpm) was eliminated by isolation of a water

TABLE 6.2

TUBE FAILURES

COMPARISON OF SURRY 2 AND TURKEY POINT 4

I. Chloride Operation

	Chloride, ppm			
	>0.2	>1	>5	>10
	Days (Approximate)			
A. Surry 2				
To 1st AVT failure (from AVT startup)	∿180	∿75	∿11	∿5
To 1st AVT failure (including phosphate)	∿560	∿360	∿180	
B. Turkey Point 4				
To 1st AVT failure (from AVT startup)	∿52	∿10	∿2	∿1
To 1st AVT failure (including phosphate)	∿277	∿100	∿50	∿28

II. Power Operations

	Calendar Months	EFPY
A. Surry 2		
To 1st phosphate failure	15	0.5
To 1st AVT failure (from AVT startup)	12	0.9
To 1st AVT failure (including phosphate)	34	1.6
B. Turkey Point 4		
To 1st phosphate failure	14	0.7
To 1st AVT failure (from AVT startup)	11	0.6
To 1st AVT failure (including phosphate)	26	1.3

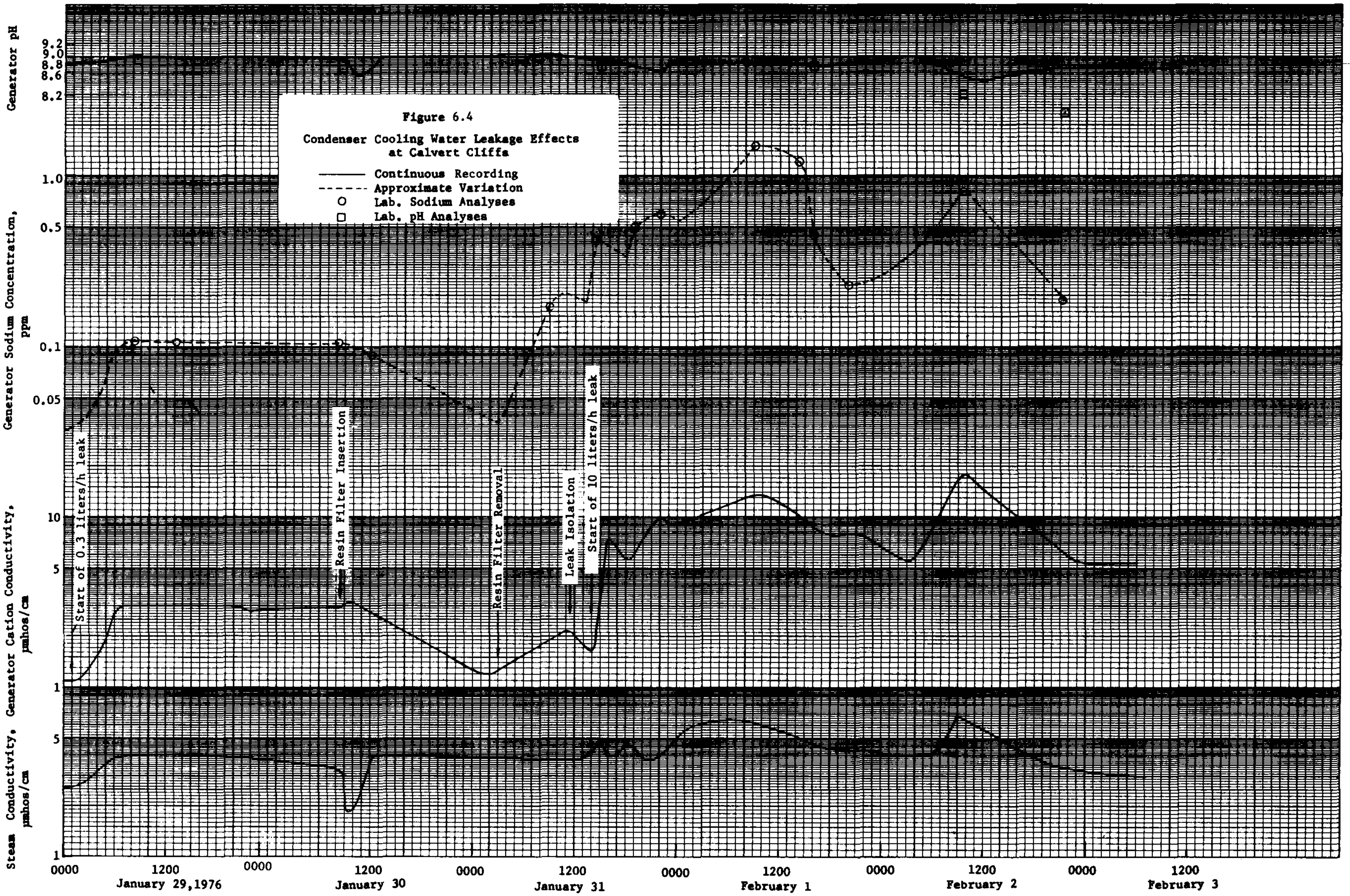


Figure 6.4
Condenser Cooling Water Leakage Effects at Calvert Cliffs

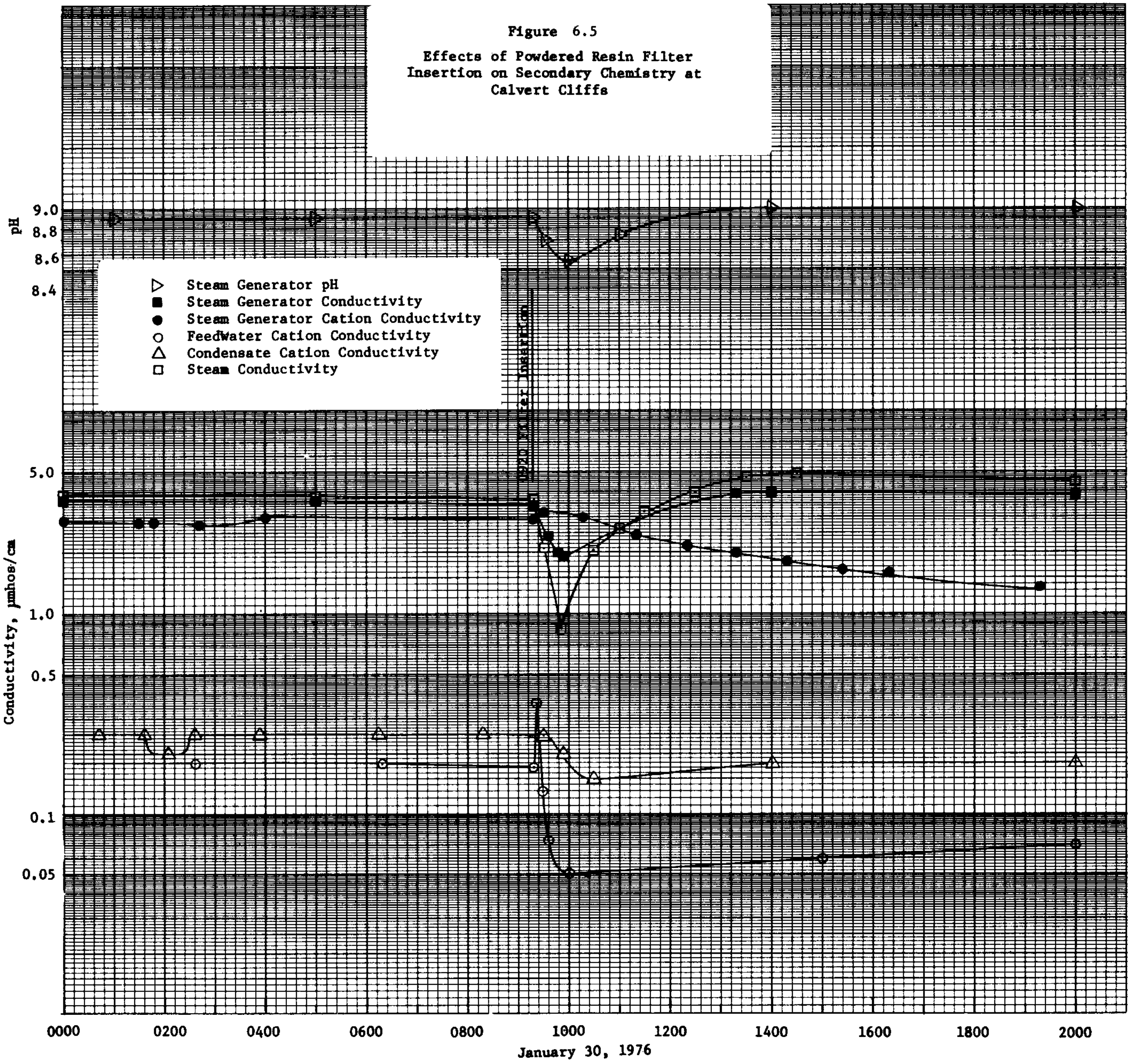


Figure 6.5

Effects of Powdered Resin Filter Insertion on Secondary Chemistry at Calvert Cliffs box at 1130 hours. Another leak of about 10 liters/h (0.045 gpm) started at ∿1400 hours resulting in a peak in cation conductivity at ∿1500 hours on January 31. The event then became more complicated with variation in blowdown rates, the location and possibly the rate of the leak, and the insertion and removal of filters and demineralizers with the possible throw of contaminants from resins. It was not possible to resolve the different effects from available data.

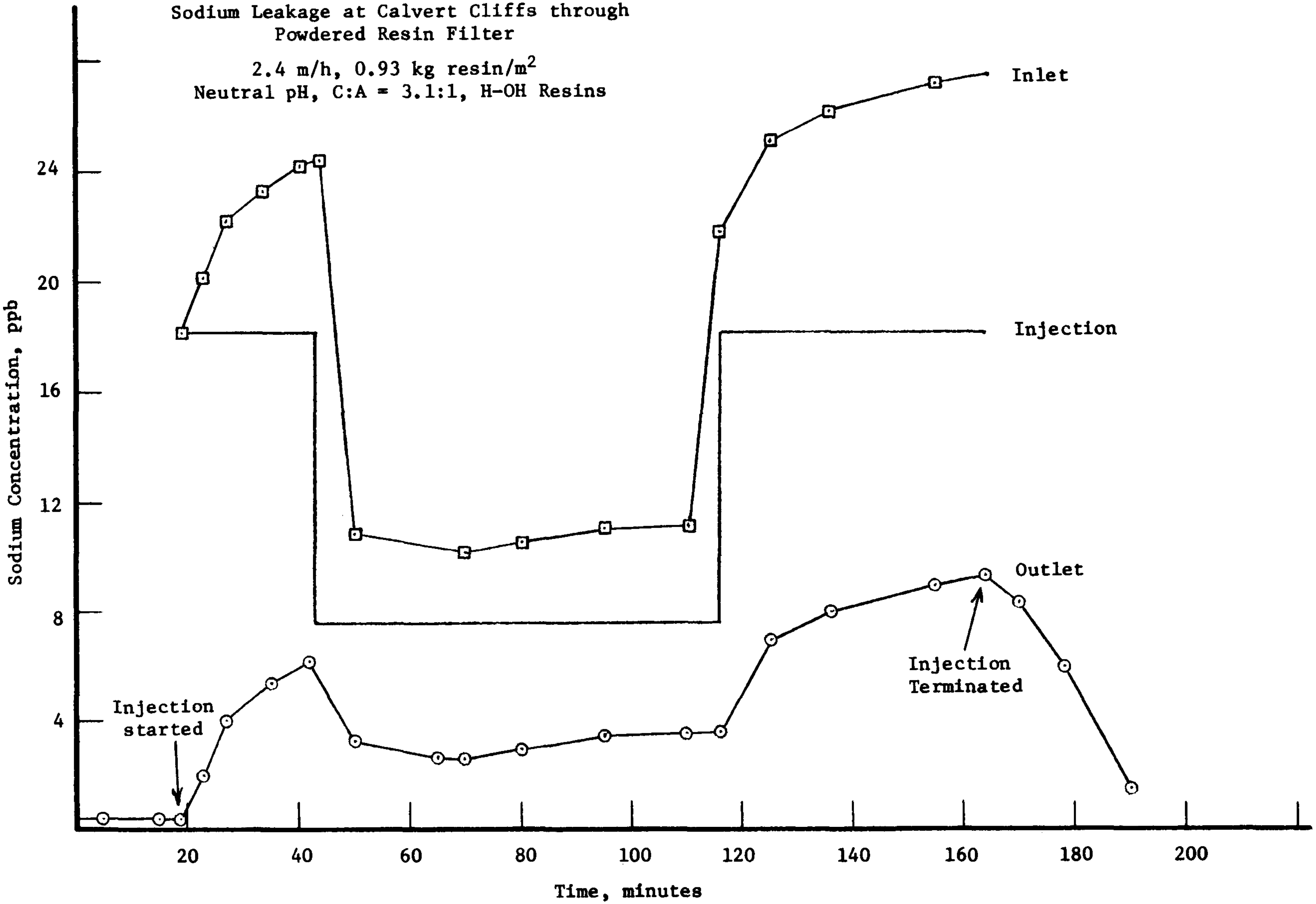
To augment plant operating data on the filters, tests were planned to determine ionic removal efficiencies of sodium and chloride as a function of precoat resin ratio, resin loading, flow rate, etc. Inspections of the general precoat characteristics prior to the test through sight glasses provided on each vessel indicated that unprecoated areas were present particularly near the filter element bottoms. In addition, precoat distribution abnormalities were noted with weld areas on the septum screens clearly outlined by the precoat wavy surfaces evident on the septums 2 to 4 rows into the array. Peak to trough differences of 0.6 to 1 cm were observed.

Nonetheless, the first test was run on March 21. Vessel 16 was precoated with 53 kg of hydrogen form cation resin and 17 kg of hydroxide form anion resin (0.93 kg/m^2 and 3.12:1 = C:A). Salt solution injection was begun to give an inlet sodium concentration of ∿10 ppb at the expected precoat flowrate of 284 m^3/h. It was subsequently determined, after sodium analyses indicated the flowrate was lower, that the actual flowrate in the precoat mode was 182 m^3/h or 2.4 m/h. Inlet and outlet sodium concentration variations are shown in Figure 6.6. Approximately 25% leakage was observed within five minutes with neutral pH feed. Reduction of the inlet sodium concentration did not reduce the percent leakage although lower effluent sodium concentrations were observed. Less than 5% of the claimed resin capacity of 2 meq/gram was exhausted during the three hour test. This exceptionally low resin utilization could have been caused by poor resin precoat distribution on the septums

Figure 6.6

Sodium Leakage at Calvert Cliffs through Powdered Resin Filter

2.4 m/h, 0.93 kg resin/m^2
Neutral pH, C:A = 3.1:1, H-OH Resins



or defective septums.

Two subsequent evaluations of the precoat filter system were conducted by BGE personnel. The first test was performed on July 14. Six precoat filters were put in service at 1025 hours and removed at 1150 hours. Figure 6.7 summarizes generator chemistry subsequent to filter insertion. The decrease in steam generator pH and specific conductivity may be attributed to precoat filter ammonia removal and/or to a pH depression from cation resin decomposition products. However, the increase in generator cation conductivity suggests that resin breakthrough caused a significant portion of the observed transient. The observation of resin in the #11 precoat filter effluent confirmed that some resin breakthrough did occur.

Cation resin is a sulfonated organic compound with an associated cation, e.g., $[\mathrm{RSO_3}]^{-}\mathrm{Na}^{+}$ or $[\mathrm{RSO_3}]^{-}\mathrm{H}^{+}$, where R denotes an organic grouping. Anion resin is an organic amine, e.g., $[\mathrm{R{-}N}\leqslant]^{+}\mathrm{Cl}^{-}$ or $[\mathrm{R{-}N}\leqslant]^{+}\mathrm{OH}^{-}$. Sodium and chloride could exist on the resin as a result of previous use during condenser leakage. On entering the feedwater, the resin begins to decompose. Sulfonic acid is the major decomposition product of the cation resin. Trimethylamine and methyl alcohol are the two major products from anion resin decomposition and would be expected to volatilize with the steam. Sulfonic acid will stay predominantly in the generators since it is a strong (highly ionized) acid. The formation of sulfonic acid groups can readily explain the observed variations in generator chemistry, i.e., pH and specific conductivity would be depressed, while cation conductivity would increase. Ammonia, bicarbonate, or hydrazine removal by the filters cannot explain the increased cation conductivity.

A second test was performed by BGE personnel on August 19. Six precoat filters were inserted at 1035 hours and removed at 1138 hours. Sodium in the filter influent and effluent, feedwater, condensate and steam generator blowdown was measured. pH and oxygen data in the feed and condensate also were reported. Results are summarized in Tables 6.3 to 6.5. Sodium

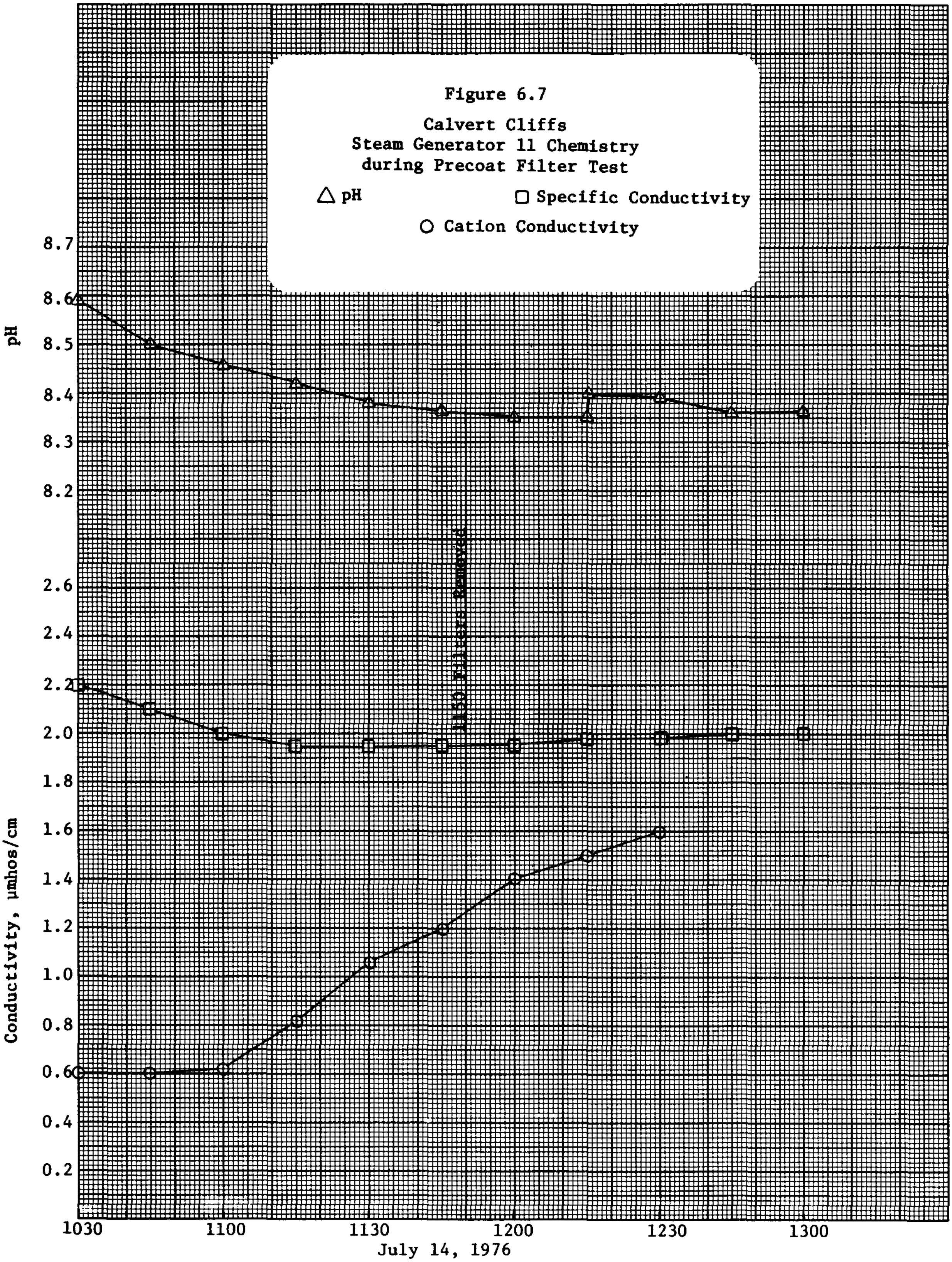


Figure 6.7

Calvert Cliffs
Steam Generator 11 Chemistry
during Precoat Filter Test

TABLE 6.3

CALVERT CLIFFS

PRECOAT FILTER INFLUENT AND EFFLUENT SODIUM

(I = Influent, E = Effluent)

Filter No.		Sodium (ppb)
11	I	NR*
	E	1.0
12	I	0.5
	E	1.2
13	I	NR
	E	1.2
14	I	0.2
	E	1.2
15	I	0.4
	E	0.7
16	I	NR
	E	2.2

*NR = Not Reported

TABLE 6.4
CALVERT CLIFFS STEAM GENERATOR SODIUM

	Sodium (ppb)	
Time	Steam Generator 11	Steam Generator 12
0930	11	9
1035	Precoat filters in service	
1138	Precoat filters removed from service	
1245	39	59
1500	26	38

TABLE 6.5

CALVERT CLIFFS CONDENSATE AND FEEDWATER CHEMISTRY

	Sodium (ppb)		Oxygen (ppb)		pH	
Time	Condensate	Feedwater	Condensate	Feedwater	Condensate	Feedwater
1022	0.40	0.69	30	17	8.80	9.10
1050	0.40	1.60	30	17	8.75	9.25
1115	0.40	1.85	30	17	8.75	9.25

increases in the feedwater and generator are evident, i.e., probable elution of sodium off the filters. The filters had been employed previously during a period of condenser leakage and as such were partially exhausted to sodium. Steam generator cation conductivity was observed to rise sharply, but data were not recorded. Although resin was not observed in the filter effluent samples, the increase in steam generator cation conductivity with an attendant decrease in condensate cation conductivity suggests that some resin breakthrough did occur. Detection of low levels of resin throw from powdered resin systems is difficult without employing resin staining techniques.

A third test was conducted on September 1. Blowdown sodium increased from ∿9 to 50 to 60 ppb within three hours of filter insertion. As in the second test, the filters had been employed previously during condenser leakage. Samples of filter effluent revealed no sign of resin bleed. The run was aborted by high pressure drops across the Y-strainers on each precoat filter. The strainers were examined, initially felt to be resin free, and replaced. Subsequent information indicates that the strainers probably had been partially plugged with resin.

From late November 1976 to the January refueling shutdown, the filters were employed for full flow condensate treatment. On initial filter insertion, sodium concentrations in the generators increased to 30 to 40 ppb but have since returned to their normal 10 ppb level. Run length has been on the order of three weeks and has been controlled by pressure drop rather than conductivity.

Site personnel indicate that Unit 1 filters are releasing only very small amounts of resin if any at all. They are currently employing a 3.5:1 cation to anion resin ratio at a total loading of 1 kg/m^2 (0.21 pounds/ft^2) with approximately 85% of the cation resin originally in the ammonia form and the remainder in the hydrogen form. With this resin mixture, they have been able to minimize pH swings in the secondary system with demineralizer insertion. Oxygen spikes in the secondary system have been minimized by preflushing with condensate. Apparently, this procedure had not been employed during previous filter insertions when large oxygen transients led to significant effects on chemistry throughout the secondary system.

Section 7

MODELING OF COOLING WATER INLEAKAGE EFFECTS ON STEAM GENERATOR CHEMISTRY

Analytical models were developed to describe the changes in solution chemistry which occur in a crevice or porous deposit where evaporation of bulk steam generator coolant to dryness occurs and in the bulk steam generator coolant as steam quality is increased along the length of the generator. The former is referred to as the isolated cavity model and the latter as the dynamic equilibrium model.

These modeling efforts were hampered somewhat by the sparsity of physical chemistry data on ionization products, solubility products, activity coefficients and gas volatilities at high temperature. The major physical chemistry parameters employed during the study are shown in Table 7.1. These properties are felt to represent the most accurate estimates of each parameter available at this time.

For the purpose of this study, cooling waters were classed in five general categories: seawater, brackish water, fresh water with alkaline forming tendency, fresh water without alkaline forming tendency, and cooling tower water. As representative of these water types, typical water analyses at five operating plants were employed (Table 7.2). For each water type, the disposition of major species identified in the cooling water was predicted analytically using both the isolated cavity and dynamic equilibrium models. To set the initial concentrations in the steam generator coolant, a condenser leak rate of 5 liters/h with a blowdown of 13620 liters/h (60 gpm) was assumed. Volatile chemical concentration was set to give a room temperature pH of 9.0. Emphasis was placed on the variation of pH with boiling. The major species for which it was necessary to consider precipitation were calcium sulfate, calcium hydroxide, and magnesium hydroxide. Volatilization of carbon dioxide and ammonia also were considered. In the latter stages of the study, variations in solution chemistry with different pH control additives such as morpholine and cyclohexylamine also were considered. Constants for the volatile

TABLE 7.1

PHYSICAL CHEMISTRY RELATIONS*

$H_2O \rightleftharpoons H^+ + OH^-$

$$\log Q = -\frac{151.713}{T} - 111.491 - 0.03685T + 44.077 \log T + \frac{5.36\sqrt{I}}{1+\sqrt{I}} - (0.6356 - 0.001078T)\, I$$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$\log Q = -6.17 + \frac{2.396\sqrt{I}}{1+1.5\sqrt{I}} \qquad \text{(at 275°C)}$$

$Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-$

$$\log K_s = -25.7085 + 12.9722 \log T - \frac{530.49}{T} - 0.032331\, T + \frac{7.722\sqrt{I}}{1+2.16\sqrt{I}} - 0.16\, I + 0.0125\, I^2$$

$Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$

$$\log K_s = \log K_{s_{Ca(OH)_2}} - 5.6$$

$HSO_4^- \rightleftharpoons H^+ + SO_4^=$

$$\log Q = 91.471 - 33.0024 \log T - \frac{3520.3}{T} + \frac{4.792\sqrt{I}}{1+1.76\sqrt{I}}$$

$CaSO_4 \rightleftharpoons Ca^{++} + SO_4^=$

$$\log K_s = -133.207 + 53.5472 \log T + \frac{3569.6}{T} - 0.0529025\, T + \frac{9.584\sqrt{I}}{1+1.5\sqrt{I}}$$

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$$-\log K = \frac{2382.2}{T} - 8.153 + 0.02194\, T$$

Where K_s = Solubility product

K = Equilibrium constant

Q = Molal product

I = Ionic strength, Molality

T = Temperature, °K

* Carbonic acid data from Reference 10; Remaining relations from Reference 11

Table 7.2

REPRESENTATIVE COOLING WATER ANALYSES

	Alkaline Fresh[a]	Neutral Fresh[b]	Brackish[c]	Cooling Tower[d]	Seawater[e]
Calcium, ppm	58	32	44	160	400
Magnesium, ppm	15	11	78	55	1272
Sodium, ppm	13	3.2	603	16	10561
Potassium, ppm	f		20		380
Lithium, ppm	f	f	f	f	0.1
Lead, ppm	f	0.004	f	f	0.21
Chloride, ppm	4.8	2.1	1053	10.5	18980
Carbonate, ppm	0	f	f	f	f
Bicarbonate, ppm	217	149	68	61	142
Total Alk., ppm $CaCO_3$	178	f	56	50	f
P-Alk., ppm $CaCO_3$	0	f	f	f	f
Fluoride, ppm	f	0.25	0.08	f	3.5
Bromide, ppm	f	f	3.5	f	65
Sulfate, ppm	45	7	220	571	2649
Thiosulfate, ppm	f	f	f	f	f
Sulfite, ppm	f	<0.1	f	f	f
Nitrite, ppm	f	0.06	f	f	0.0001-0.05
Nitrate, ppm	f	1.6	1.2	f	0.001-0.7
Phosphate, ppm	f	0.6	f	f	>0.001-0.1
Iodide, ppm	f	f	f	f	0.05
Silica, ppm	14	5	8.6	25	0.01-7.0
Cabon Dioxide, ppm	f	3.8	2.9	f	6
Oxygen, ppm	f	f	6.2	f	5
Turbidity, JTU	2.5	f	f	f	f
pH	7.9	f	f	f	7.5-8
Conductivity, μmhos/cm	455	f	f	f	f
T.D.S., ppm	297	f	2100		34500

[a] Based on Mississippi River water analysis at Prairie Island on January 21, 1972.

[b] Based on 1 year average of Lake Michigan analyses.

[c] Based on Surry analysis data adjusted to 1000 ppm chloride concentration.

[d] Based on Lake Michigan analysis with a tower concentration factor of 5 and sulfuric acid addition for scaling control.

[e] Normal seawater analysis.

[f] To be determined.

additives are given in Table 7.3. A general description of the two models and results describing solution chemistry variations during evaporation in each model geometry are presented below. A detailed description of the physical chemistry considerations and mathematical procedures employed to solve the equations governing the phenomena is given in Appendix A. Also included in Appendix A is a listing of the computer programs for the two models.

Isolated Cavity Model

In the isolated cavity model, a mass of steam generator bulk water is boiled to dryness in a cavity. Additional liquid is not allowed to enter the cavity to dilute the concentrated solution which results from boiling. Steam vapor is allowed to exit the cavity as it is generated. As the solution is boiled away, volatile species enter the steam phase and are removed from the liquid in the cavity. Salts such as calcium sulfate, calcium hydroxide, and magnesium hydroxide precipitate. In the results presented herein redissolution of previously precipitated salts is allowed, i.e., total equilibrium of all species within the liquid phase including solid precipitates is assumed. The model would be readily modifiable to eliminate redissolution of species precipitated early in the evaporation process. However, this effect is not expected to lead to any significant changes in the results at high concentration factors. The concentration factor is defined as the ratio of the initial solution volume to remaining solution volume, i.e., the concentration factor would be 10 if a 10 gram sample were evaporated to the point where one gram of liquid remained in the cavity.

Concentrations of major species for each of the water classes are given in Table 7.4 as a function of concentration factor. These results were obtained using ammonia as a pH control additive. The five cooling waters fall into two general classes: acid or caustic forming. Seawater, brackish water, and cooling tower water form concentrated acid solutions on boiling in the isolated cavity. Both fresh water types form sodium hydroxide solu-

TABLE 7.3
VOLATILE CHEMICAL PROPERTIES

	Ammonia	Cyclohexylamine	Morpholine
At 25°C			
Concentration, ppm	0.25	1	5
pH	9	9	9
Ionization constant	$1.77(10^{-5})$	$4.39(10^{-4})$	$2.13(10^{-6})$
At 280°C			
$K_D\ (\frac{\text{ppm in steam}}{\text{ppm in solution}})$	3.7[a]	12.5[b]	0.5[c]
Ionization constant	$6.76(10^{-7})$[d]	$3.0(10^{-6})$[e]	$6(10^{-7})$[e]

[a] Reference 12

[b] Reference 13

[c] Reference 14, assumed independent of temperature and concentration

[d] Reference 11

[e] Reference 15, corrected for ionic strength

TABLE 7.4

IONIC CONCENTRATIONS IN SOLUTIONS AT 280°C*

ppm

	Local Concentration Factor in Steam Generator						
	1	2	5	10	100	1,000	10,000
Alkaline Fresh							
Bicarbonate	0.08	∿0	∿0	∿0	∿0	∿0	∿0
Bisulfate	0.004	0.008	0.013	0.016	0.027	0.0007	0.0003
Calcium	0.02	0.043	0.11	0.21	2.1	14.6	17.9
Chloride	0.0018	0.0036	0.009	0.018	0.18	1.8	18
pH	5.90	5.92	6.14	6.37	7.13	8.01	8.35
Magnesium	0.0055	0.011	0.028	0.055	0.0106	0.00015	∿0
Sodium	0.005	0.01	0.02	0.05	0.5	4.8	48
Sulfate	0.013	0.025	0.07	0.15	1.62	0.4	0.5
Neutral Fresh							
Bicarbonate	0.055	∿0	∿0	∿0	∿0	∿0	∿0
Bisulfate	0.0007	0.0014	0.0027	0.0033	0.0063	0.0013	0.0002
Calcium	0.012	0.024	0.06	0.12	1.2	10.9	30.6
Chloride	0.0008	0.0015	0.004	0.008	0.08	0.8	7.8
pH	5.87	5.82	5.99	6.23	6.97	7.85	8.24
Magnesium	0.004	0.008	0.02	0.04	0.023	0.0003	∿0
Sodium	0.0012	0.0024	0.006	0.012	0.12	1.2	12
Sulfate	0.002	0.0038	0.01	0.022	0.25	0.5	0.27

TABLE 7.4 (continued)

	Local Concentration Factor in Steam Generator						
	1	2	5	10	100	1,000	10,000
Brackish							
Bicarbonate	0.03	∿0	∿0	∿0	∿0	∿0	∿0
Bisulfate	0.002	0.047	0.93	0.14	1.2	13.9	214
Calcium	0.016	0.032	0.081	0.16	1.1	0.78	2
Chloride	0.4	0.8	1.9	3.9	39	390	3870
pH	5.85	5.78	5.87	6.04	5.92	5.30	4.37
Magnesium	0.03	0.06	0.14	0.29	2.3	21.8	208
Sodium	0.23	0.45	1.1	2.3	22.6	226	2260
Sulfate	0.06	0.12	0.3	0.67	5.6	30	214
Cooling Tower							
Bicarbonate	0.02	∿0	∿0	∿0	∿0	∿0	∿0
Bisulfate	0.054	0.11	0.23	0.32	1.3	22.4	342
Calcium	0.06	0.12	0.3	0.6	0.6	0.16	0.1
Chloride	0.004	0.008	0.02	0.04	0.4	3.9	39
pH	5.87	5.82	5.95	6.11	6.05	5.53	4.88
Magnesium	0.02	0.04	0.1	0.2	1.5	12.9	114
Sodium	0.006	0.012	0.03	0.06	0.6	5.9	59
Sulfate	0.16	0.31	0.83	1.8	7	46	353

TABLE 7.4 (continued)

	Local Concentration Factor in Steam Generator						
	1	2	5	10	100	1,000	10,000
<u>Seawater</u>							
Bicarbonate	0.05	0	0	0	0	0	0
Bisulfate	0.19	0.31	0.84	1.9	23	370	5860
Calcium	0.15	0.3	0.7	1.1	1	4.7	108
Chloride	7	14	35	70	700	6960	69600
pH	5.965	6.03	5.93	5.77	5.09	4.03	2.48
Magnesium	0.47	0.94	2.2	4.3	42	400	3700
Sodium	4	8	19.8	39.6	400	3960	39600
Sulfate	0.78	1.6	4.0	6.9	41	263	630

*Blowdown 13620 1/h (60 gpm)
Leak Rate 5 1/h (0.022 gpm)

tions upon boiling. Hydrochloric acid is formed with seawater and brackish water. Sulfuric acid is formed with the cooling tower waters treated for carbonate control. Variations in pH with boiling are shown in Figure 7.1 for alkaline fresh and seawater cooling waters. As can be seen, pH is depressed approximately two full units at a concentration factor of 10^3 for the seawater case; pH in the isolated cavity is increased greater than two full units at a concentration factor of 10^3 with alkaline fresh water.

Using the model, it is possible also to evaluate the difference in isolated cavity solution chemistry with variation in pH control additive. Differences in the pH with ammonia, cyclohexylamine, and morpholine additives are shown in Figures 7.2 and 7.3 for the alkaline fresh water and seawater cases, respectively. These cases bound the variation expected with other cooling water types. In the fresh water cooled case, morpholine which is less volatile than ammonia or cyclohexylamine, initially produces a pH about 0.2 units higher than the other additives. This difference becomes insignificant when the local concentration factor is greater than 20. The model predicted similar effects among the various amines in the seawater cooled plant but with less initial pH difference (Figure 7.3). As magnesium began to precipitate in the seawater cases, pH variation was almost identical in solutions of different amines.

Dynamic Equilibrium Model

Recognizing that the isolated cavity model was not applicable to describing the dynamic vapor to liquid equilibrium which exists in the steam generator bulk fluid as the coolant is boiled to higher qualities, a second model was developed. In this model, the total mass in the control volume is maintained constant while the liquid mass is reduced, i.e., the vapor quality and mass are increased. In the absence of cooling water ingress, steam generator pH (at 25°C) varied with local steam quality as shown in Figure 7.4. The predicted pH variation at 280°C in the bulk coolant is shown in Figure 7.5 and 7.6 for fresh water and seawater inleakage, respec-

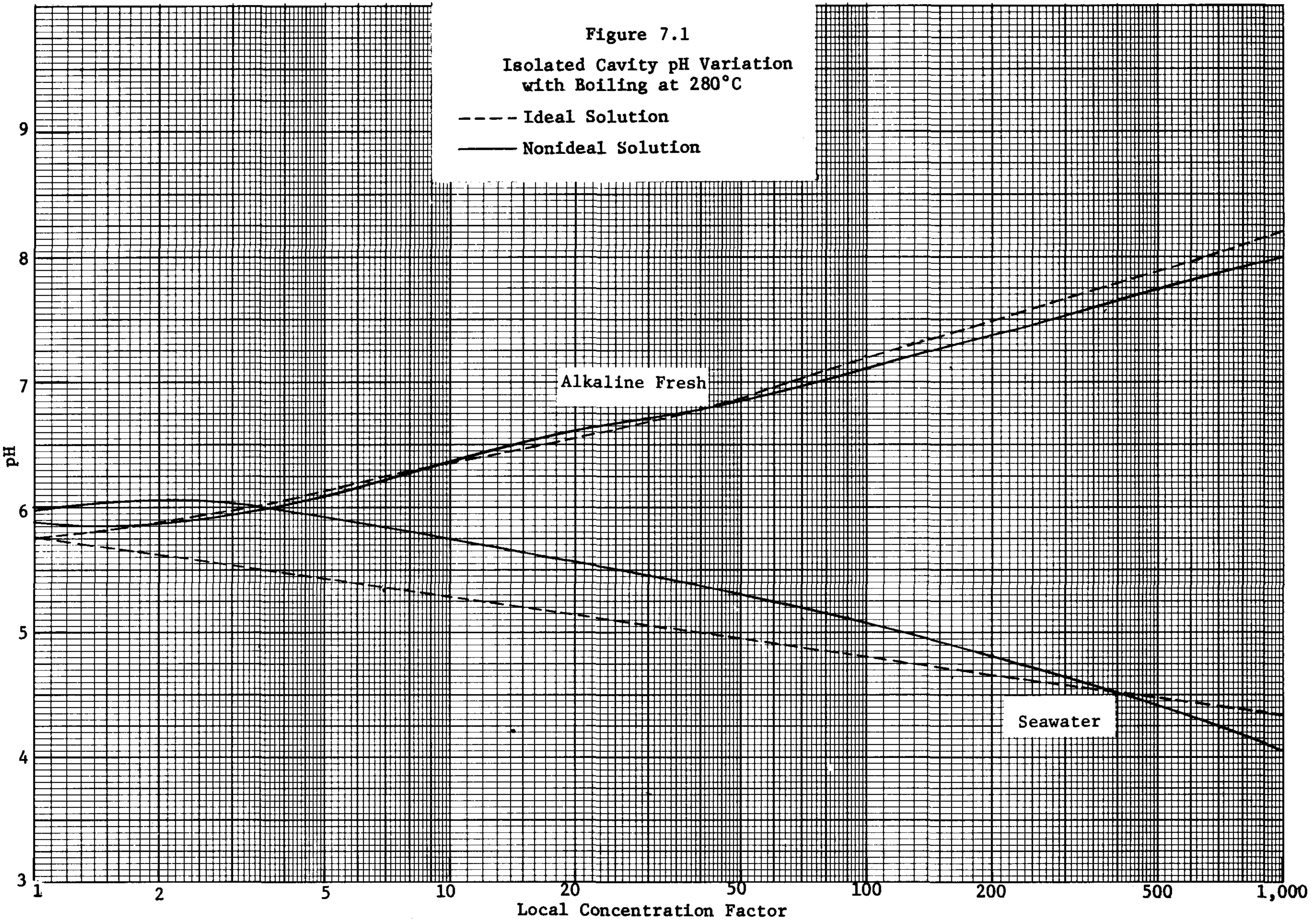


Figure 7.1

Isolated Cavity pH Variation with Boiling at 280°C

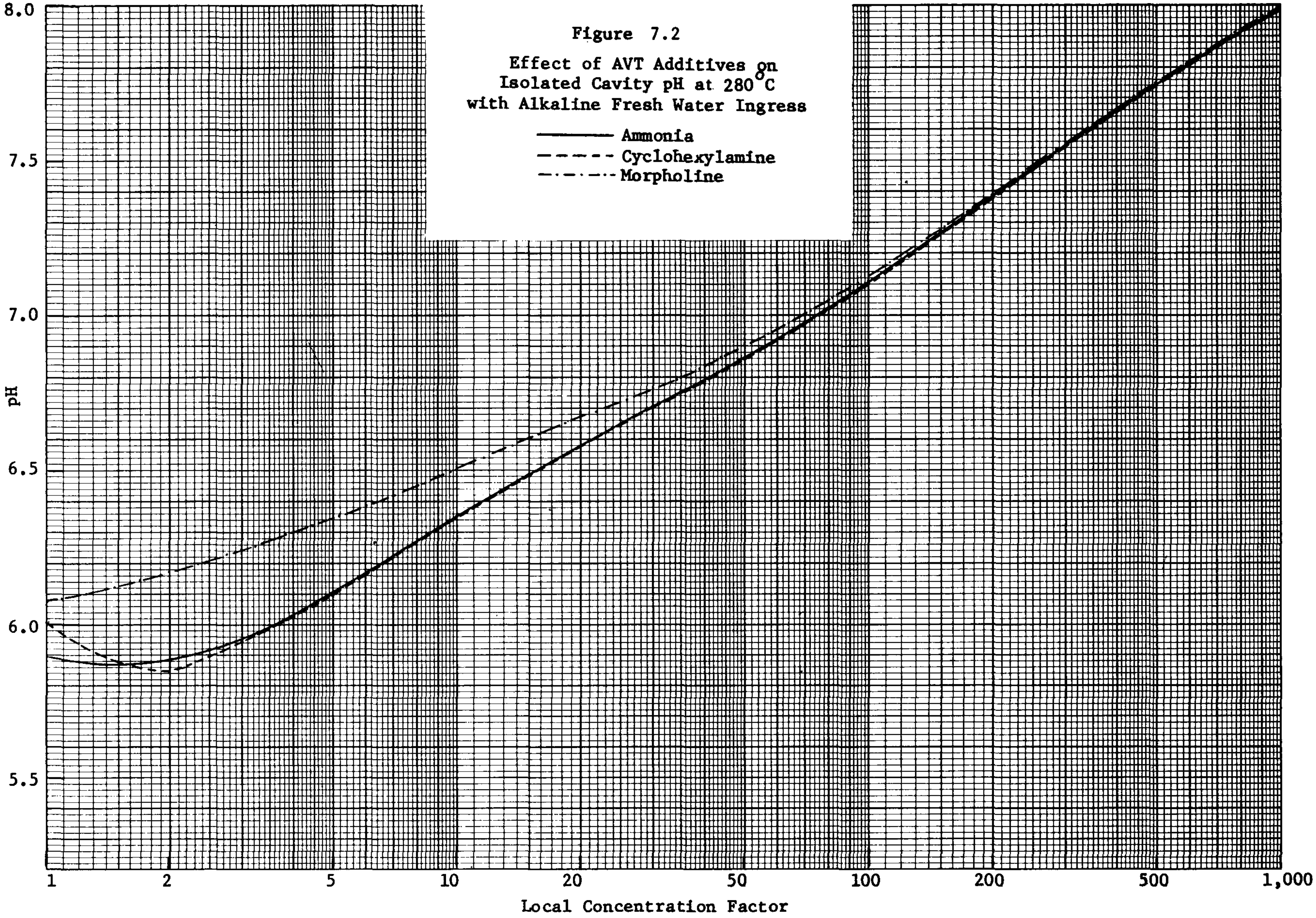


Figure 7.2

Effect of AVT Additives on Isolated Cavity pH at 280°C with Alkaline Fresh Water Ingress

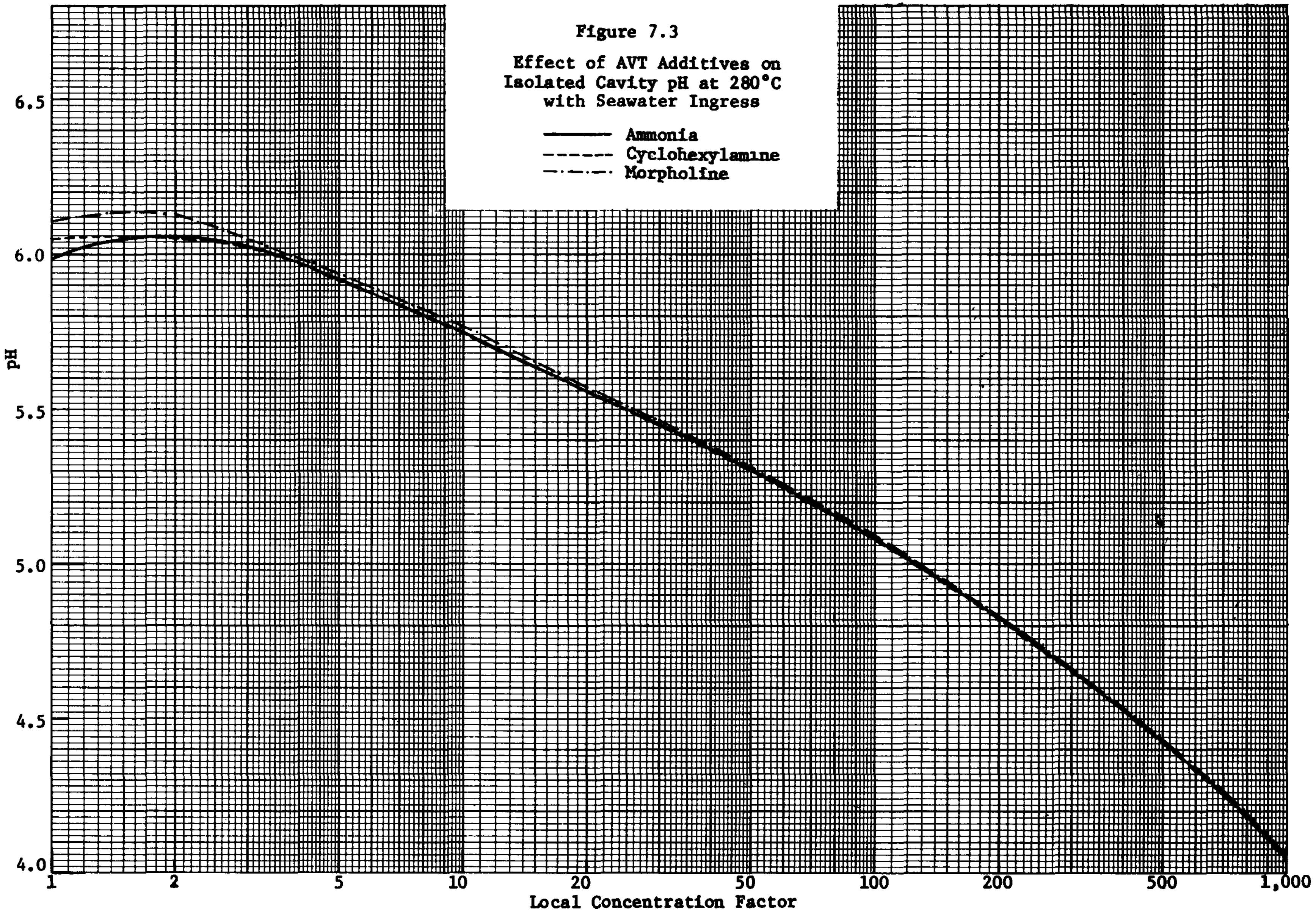


Figure 7.3

Effect of AVT Additives on Isolated Cavity pH at 280°C with Seawater Ingress

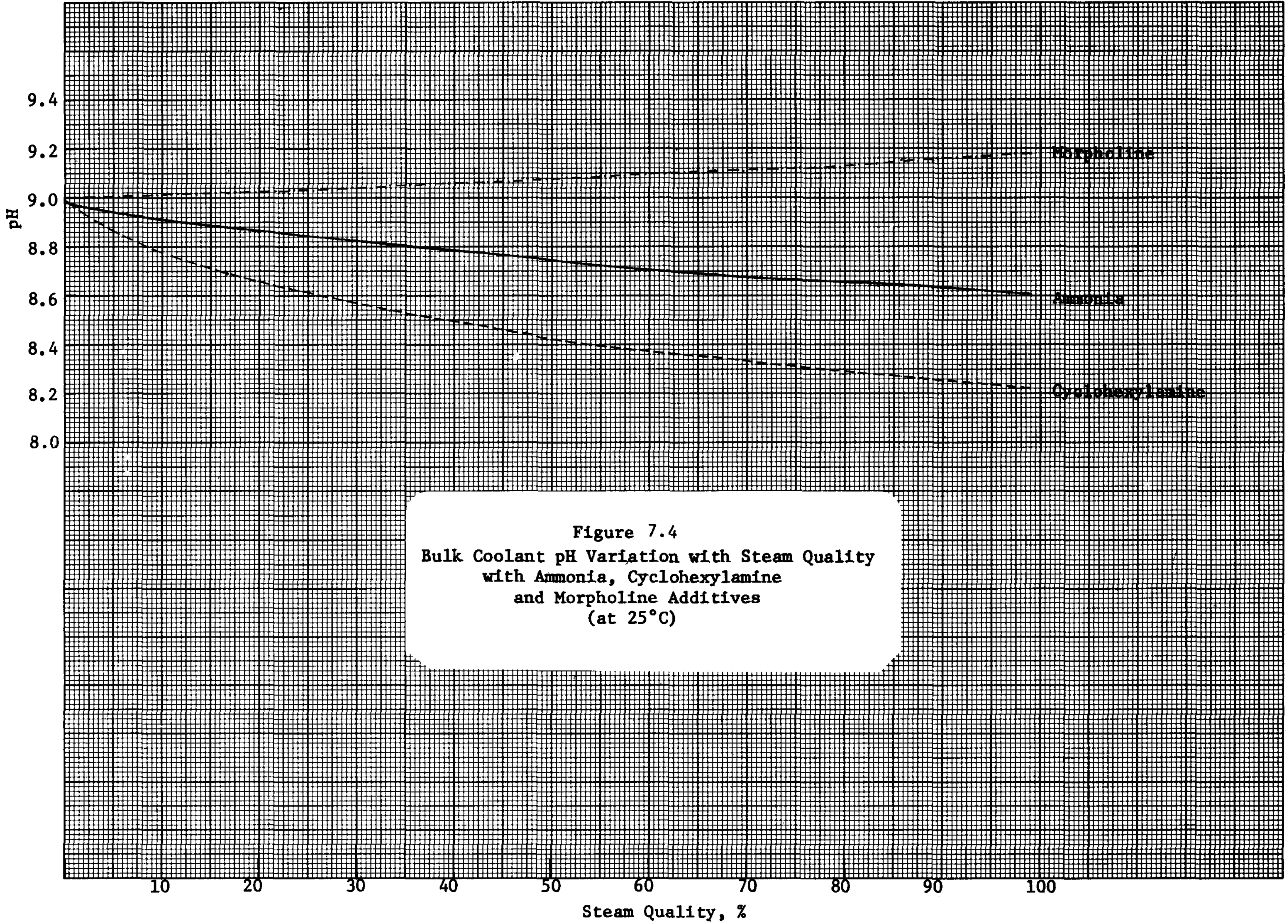


Figure 7.4
Bulk Coolant pH Variation with Steam Quality
with Ammonia, Cyclohexylamine
and Morpholine Additives
(at 25°C)

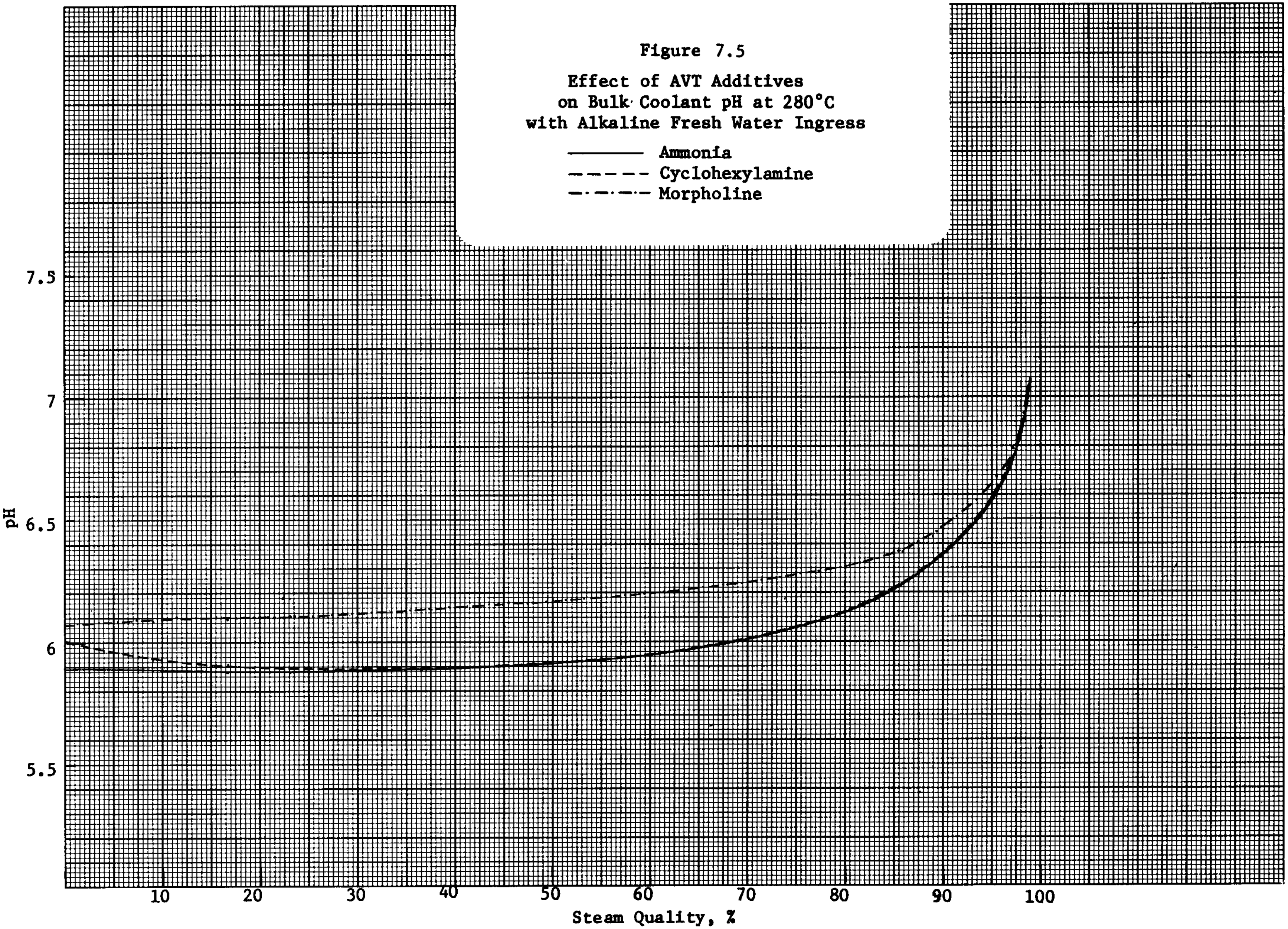


Figure 7.5

Effect of AVT Additives on Bulk Coolant pH at 280°C with Alkaline Fresh Water Ingress

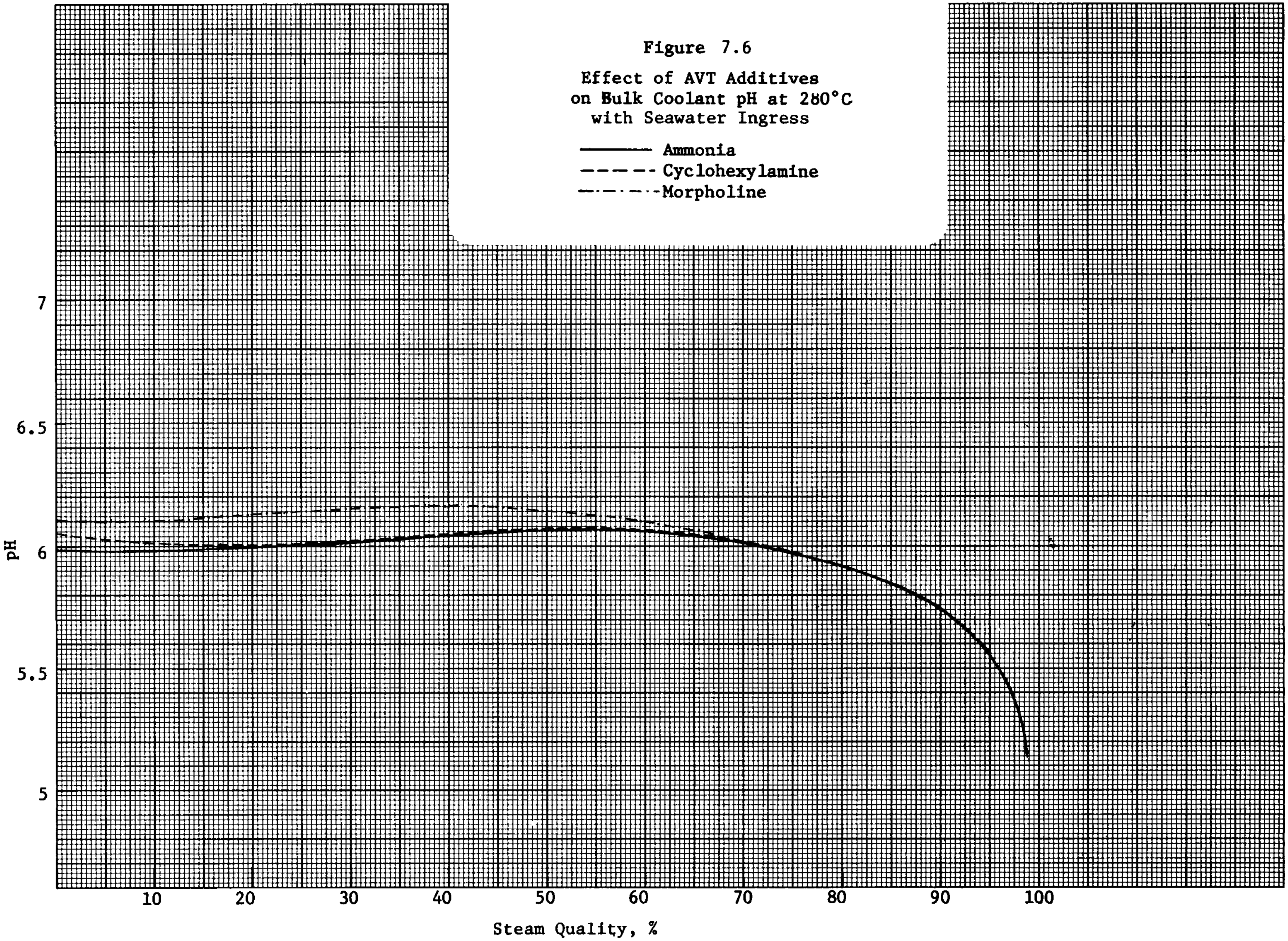


Figure 7.6

Effect of AVT Additives on Bulk Coolant pH at 280°C with Seawater Ingress tively, as a function of local steam quality and designated amine. In general, pH decreases are predicted to occur in the bulk coolant with seawater ingress and pH increases with fresh water ingress. The general trends of the model were similar to those which were developed in the isolated cavity model.

Implications of the Models

It is recognized that significant inaccuracies can be present in the physical chemistry parameters employed in developing the models. In addition, species interactions which are not recognized in the model could be occurring. In particular, reactions of silica, metal oxides, and metal have not been considered to date. Nonetheless, certain general implications can be drawn from the modeling results. First, during condenser inleakage highly acidic solutions will be formed in plants using seawater and brackish coolants during the process of evaporation in regions where local evaporation of the bulk coolant to near dryness can occur. Some neutralization of these solutions could result from dissolution of metal oxides or metals surrounding or forming the cavity. In any event, the acidic solutions, generically hydrochloric acid, would be expected to lead to aggressive corrosion in such areas. That ferrous chloride solutions can lead to aggressive attack of carbon steel materials at steam generator temperatures has been demonstrated by Potter and Mann.[16] In their experiments, the rapid growth of non-protective magnetite was observed in 0.1 molar ferrous chloride solutions at 300°C. Ferrous chloride would be expected to result from corrosion of support plates where crevices are formed with the tubes if such crevices function even intermittently as isolated cavities. In a cooling tower plant, the formation of sulfuric acid in local areas is to be expected. However, the local corrosion rate would not be expected to be as high as that for the seawater case in that similar concentrations of ferrous sulfate and ferrous chloride would exhibit markedly different pH levels. For example, a 0.1 molar solution of ferrous chloride has a pH of approximately 3.0 at 300°C whereas that of a 0.1 molar solution of ferrous sulfate is approximately 5. Recognizing that salts of strong acids generally lead to corrosion rates similar to those of the strong acid itself at a similar pH[17], carbon steel corrosion in the chloride solution from seawater would be expected to be significantly more rapid than in the sulfate solution from the cooling tower water.

In fresh water plants, the predicted behavior of Lake Michigan and Mississippi River water were nearly identical although in the past the Lake Michigan water has been designated as a neutral water and the Mississippi River water an alkaline water. These classifications were developed without consideration of the effects of carbon dioxide volatility and are not supported by the model results. Based on the current models, both waters would be expected to lead to significant pH elevations in an isolated cavity and in the bulk fluid as boiling progresses. High rates of carbon steel corrosion are not expected until percent level solutions of hydroxide develop.[18] At a concentration factor of 10,000, sodium hydroxide concentrations were approximately 20 ppm and 60 ppm in the Lake Michigan and Mississippi River water cases, respectively.

Section 8

STEAM GENERATOR SLUDGE ANALYSES

Sludge samples obtained during steam generator lancing were received from Turkey Point (∿20 grams), Prairie Island 1 (∿200 grams), and Prairie Island 2 (∿40 grams). Analyses for major corrosion products and calcium and magnesium were completed on the Turkey Point and Prairie Island 1 samples. Concentrations of phosphate also were determined on the Prairie Island 1 samples after dissolution in nitric acid. Results are presented in Table 8.1. Westinghouse sludge analyses for Turkey Point 4 and Prairie Island 1 are presented for comparison.

At Turkey Point 4, a relative increase in iron and copper concentration in the sludge with time is evident along with decreases in nickel, calcium, and magnesium. The depletion in cooling water hardness species can be attributed to either reduced cooling water ingress or gradual removal of phosphate sludge residuals rich in these species. A total mass balance on the samples suggests a reduction of copper oxidation state with the transition to AVT. However, available data are not extensive enough to verify this premise. Analyses have not yet been performed on the Prairie Island 2 sludge. It is currently planned to complete analyses on the Turkey Point and Prairie Island 2 sludge and to augment these results with sulfate analyses on all samples.

Emission spectrographic results on blowdown samples from Prairie Island 1 and 2, Surry 2, and Turkey Point 4 are given in Table 8.2. As expected, iron was the major species present in the blowdown sample at each plant. At Turkey Point 4, copper, nickel and zinc levels varied from 0.6 to 1.4%, 4.2 to 4.9%, and 5.2 to 5.5%, respectively, of the iron levels. Lead was present at the 500 to 900 ppm level. At Surry 2, results varied considerably with copper, nickel, and zinc levels reported at 1.3 to 25%, 3 to 13%, and 1.9 to 8.1%, respectively, of the iron level. Lead varied from 200 to 2400 ppm.

TABLE 8.1

SLUDGE ANALYSES

(Weight Percent)

	Iron	Nickel	Copper	Zinc	Calcium	Magnesium	Chloride	Phosphate	Sulfate
Turkey Point 4									
August 1974[a]	20	7.4	7.6	6.3	3.1	0.75	0.006	9.19[b]	0.55
May 1975[a]	29	4.3	30	7.1	0.8	0.75	NA	4.29[b]	0.03
November 1975	33.1	1.7	44.8	3.5	0.14	0.27	NA	NA[c]	NA[c]
May 1976, SG 4B	36.9	0.4	35	NA	0.35	0.29	NA	NA[c]	NA[c]
Prairie Island 1									
September 1974, SG 11[a]	42.6	0.3	0.08	NA	10.5	1.9	NA	26.0	NA
September 1974, SG 12[a]	39.9	0.3	0.11	NA	13.7	2.7	NA	26.7	NA
June 1976, SG 11	63.6	0.4	1.6	NA	1.7	1.0	NA	0.5	NA[c]
June 1976, SG 12	59.6	0.6	2.9	NA	2.1	0.6	NA	0.5	NA[c]

a) Westinghouse analyses

b) Phosphorus analyses reported by Westinghouse converted to phosphate equivalent

c) NA - No analysis

TABLE 8.2A

PRAIRIE ISLAND 1 & 2

COMPOSITION OF STEAM GENERATOR BLOWDOWN FILTERABLES

Steam Generator	11	11	12	12	21	22	22
Chromium	0.31%	0.30%	0.27%	0.27%	0.46%	0.57%	0.45%
Manganese	0.43%	0.32%	0.70%	0.31%	0.27%	0.36%	0.56%
Iron	81%	79%	81%	73%	94%	89%	87%
Cobalt	<330.	<257.	<277.	<238.	<317.	<286.	<305.
Nickel	1.2%	0.66%	1.2%	0.62%	0.56%	0.70%	0.91%
Copper	0.21%	0.45%	0.13%	0.19%	0.15%	0.18%	0.19%
Zinc	508.	432.	693.	361.	0.10%	808.	488.
Mercury	<29.	<22.	<26.	<21.	<23.	<25.	<24.
Lead	0.12%	0.14%	696.	0.13%	727.	0.11%	454.
Arsenic	<27.	<24.	<23.	<20.	<21.	<23.	<21.
Silver	<145.	287.	<139.	≤246.	≤100.	≤171.	<200.
Cadmium	≤194.	<105.	<139.	≤150.	<100.	<171.	<200.
Titanium	<895.	<908.	<823.	<720.	1.2%	1.6%	1.9%
Tin	<205.	<215.	<255.	<190.	<250.	<470.	<366.
Sample Period	11/28 to 11/30/75	1/9 to 1/11/76	11/13 to 11/15/75	11/21 to 12/24/75	11/19 to 11/20/75	11/15 to 11/17/75	1/28 to 1/30/76

Concentrations in ppm unless otherwise stated.

TABLE 8.2B

SURRY 2

COMPOSITION OF STEAM GENERATOR BLOWDOWN FILTERABLES

Sample Identification Element	VSGA-5 1313 (8-4) 441-3-164	VSGA-9 (8-13) 441-3-168	VSGA-15 0900 (8-27) 441-3-174	VSGA-26 0800(9-26) 441-3-185	VSGA-33 0855(10-15) 441-3-192	VSGA-38 1010(10-29) 441-3-197	VSGC-5 1313(8-4) 441-3-236	VSGC-26 0800(9-26) 441-3-257	VSGC-33 0855(10-15) 441-3-264
Cr (%)	.34	.35	.39	.39	.17	.30	.30	.36	.32
Mn (ppm)	.13%	909	.15%	809	.18%	.18%	.13%	.15%	.17%
Fe (%)	73	74	68	61	48	62	59	77	57
Co (ppm)	<421	<377	<357	<313	<500	<471	<318	<305	<434
Ni (%)	4.7	3.8	4.2	2.9	6.4	5.7	2.8	2.3	4.2
Cu (%)	2.1	1.6	.88	3.3	12	4.2	2.4	1.3	10
Zn (%)	3.3	2.9	3.2	2.5	3.9	4.4	1.3	1.5	2.0
Hg (ppm)	<48	<33	<37	<34	<51	<41	<33	<35	<40
Pb (ppm)	.19%	.18%	.21%	.19%	228	912	.24%	.21%	597
As (ppm)	<38	<29	<30	<30	<45	<39	<31	<29	<35
Ag (ppm)	<203	<189	<300	<145	<332	<356	<171	<207	<236
Cd (ppm)	<203	<189	≤300	<145	<332	<356	<171	<207	<236
Ti (ppm)	<.10%	<957	.16%	≤.11%	<516	<.11%	<800	.15%	<.11%
Sn (%)	.21	.22	.28	.15	.33	.27	965 ppm	.19	.17
Zr (ppm)	---	---	---	---	---	---	---	---	---

TABLE 8.2C

TURKEY POINT 4

COMPOSITION OF STEAM GENERATOR BLOWDOWN FILTERABLES

Sample Identification	TP-2Y 4A s/g 2030 (10-10)	TP-5Y 4A s/g 2100 (10-17)	TP-6Y 4A s/g 2000 (10-20)	TP-11Y 4A s/g 2130 (10-31)
Element	441-3-46	441-3-49	441-3-50	441-3-55
Cr (%)	.53	.41	.43	.37
Mn (ppm)	860	627	286	792
Fe (%)	62	59	62	63
Co (ppm)	<350	<467	<500	<516
Ni (%)	4.4	4.5	4.9	4.2
Cu (%)	1.0	1.4	1.1	.64
Zn (%)	5.3	5.5	5.4	5.2
Hg (ppm)	<35	<52	<47	<48
Pb (ppm)	545	548	926	606
As (ppm)	<33	<45	<40	<39
Ag (ppm)	<220	<278	<278	<266
Cd (ppm)	<220	<278	<278	<266
Ti (ppm)	⩽.10%	⩽.11%	.22%	⩽.10%
Sn (%)	.59	.38	.34	.37
Zr (ppm)	.19%	869	---	---

At Prairie Island 1 and 2, all ferrous alloy plants, copper was present at a level of approximately 0.1% of the iron level. Lead was present at the 500 to 1400 ppm level. Site personnel have suggested that the source of copper is the turbine after a preliminary discussion with the vendor. The major source of lead has not been identified to date.

Section 9

STEAM GENERATOR INSPECTIONS

Eddy Current Inspections

Steam generator tubing eddy current inspections at the study plants through 1976 are discussed below. The majority of tubes were inspected only through the first support plate of the hot leg side. Early U-bend inspections were limited to peripheral tubes until significant attack was noted in locations other than near the tube sheet. Initially, any tube with an indication of 50% or greater wall penetration was plugged. This plugging limit was later reduced to 40% at Surry 2 and Turkey Point 4 as a precaution.

Calvert Cliffs: A baseline preoperational eddy current inspection of 100% of accessible tube area was performed at Calvert Cliffs 1. A second inspection was performed in January 1977 after approximately 1-1/2 years of operation. Site personnel reported that no tube degradation was noted.

Prairie Island 1 and 2: A summary of the steam generator inspections is given in Table 9.1. Both units have had 3 eddy current inspections of which the first at Prairie Island 2 was a 100% baseline preoperational inspection. After over two years of operation with AVT, no tube degradation has been noted in any of the steam generators.

Surry 2: Eddy current inspection history at Surry 2 is summarized in Table 9.2. Surry 2 began operation in March 1973, had a steam generator inspection and cleaning (water lancing) in April 1974, and shut down again in September for a second inspection and cleaning prior to the change to AVT. Inspections focused on steam generator A and only through the first support plate since the main damage seen during operation with phosphate was wall thinning in the area immediately above the tube sheet. Although up to that time steam generator B required the largest number of

TABLE 9.1

EDDY CURRENT TUBE EXAMINATIONS

PRAIRIE ISLAND UNITS 1 and 2

(400 Khz)

Inspection Date	Steam Generator	Tubes Probed				Eddy Current Signals 20%		Tubes Plugged
		Inlet		Outlet				
		FS	UB	FS	UB	HL	CL	
Unit 1								
9/74	11	400	68	0	49	0	0	0
	12	936	145	435	34	0	0	0
10/74 Change to AVT chemistry.								
4/75	11		166		80	0	0	0
	12		166		80	0	0	0
3/76	11		189		128	0	0	0
	12		262		138	0	0	0
Unit 2								
9/74	21	Nominal 100% Baseline				0	0	0
	22					0	0	0
12/75	21		141		72	0	0	0
	22		137		72	0	0	0
11/76	21		257		72	0	0	0
	22		258		72	0	0	0

FS = Through first support plate
UB = Through seventh support plate (some around U-bend)
HL = Hot leg
CL = Cold leg

TABLE 9.2

EDDY CURRENT TUBE EXAMINATIONS

SURRY 2

(400 Khz)

		Tubes Probed				Eddy Current			
		Inlet		Outlet		Signals ≥20%		Tubes	Leaking
Date	SG	FS	UB	FS	UB	HL	CL	Plugged	Tubes
5/74	A	936	229	468	0	57	0	5	
	B	936	0	0	0	83		8	
	C	936	0	0	0	64		0	
7/74	B	0	60	0	0	6		6	1
9/74	A	905	92	468	50	70	0	10	
	B	928	73	0	94	68	0	19	
	C	936	77	0	50	151	0	10	
1/75 Change to AVT Chemistry									
5/75	A	545	25	237	0	74	0	35	
	B	591	17			82		29	
	C	951	20			53		68	
1/76	C	Details unavailable						2	2
2/76								42	1
3/76	C							115	1
5/76	A	670	33	0	0	52		104	
	B	801	148	0	0	101		102	
	C	985	28	0	0	134		21	
10/76	A	Details unavailable						156	6
	B							151	
	C							104	4
12/76	A							2	2

FS = Through first support plate
UB = Around U-bend
HL = Hot leg
CL = Cold leg

tubes to be plugged (>50% damage indication), steam generator C appeared to have the most incipient damage.

The first inspection after conversion to AVT was made in May 1975. Although a large number of tubes were plugged at that time (132 tubes), 84 of those tubes were in the 40 to 50% indication range and were plugged only because the criteria for plugging was changed from ≥50% to ≥40%.

In the fall of 1975 the phenomenon of denting had been noted at Turkey Point 4. Surry 2 was forced to shut down three times in early 1976 because of primary to secondary leaks in C steam generator. Because of the location of the leaks in the first two rows in hard spot regions (support plate sections between flow slots), all of the hard spot regions were plugged during the February 1976 outage (42 tubes). An additional grouping in the first three rows at and near the hard spot regions was plugged in March 1976 (115 tubes).

The extent of the denting became obvious in May 1976. At this time, eddy current testing did not show significantly greater wastage than had been noted previously. A total of 75 tubes required plugging based on plugging all tubes with ≥40% indication. Because of the extensive denting, however, the normal eddy current probe could not be used for all of the inspection because of the difficulty of passing it through many of the dents. Therefore, a special examination with a 1.37 cm probe was carried out in B generator on an additional 774 inlet and 587 outlet tubes to determine the extent of denting. Although the results are not available, an additional 66 tubes in both A and B steam generators were plugged in hard spot areas.

To improve the understanding of the denting problem, Westinghouse removed a section of the top tube support complete with two tube segments during this outage. Laboratory reports indicate that the annulus between the tube and support plate was filled with a hard corrosion product that expanded volumetrically to exert sufficient forces to dent the tube diametrically and to crack tube support plate ligaments between the tube holes and the water circulation flow holes.

On September 15, steam generator 2A developed a primary to secondary leak (about 18 m^3/h) causing a unit shutdown. The leaking tube was located at row 1 next to the tube that had been plugged in a hard spot area. The leak was located in the U-bend area. The damaged tube along with 8 other tubes in row 1 were cut out above the seventh support plate. The leak was found to result from an axial intergranular stress corrosion crack (∿11.5 cm in length) in the U-bend of the tube near the top. Five of the eight additional tubes examined showed significant ovalization with four having cracks on the inner surface (primary side). The tubes that had defect indications were located near the middle of the flow slot.

The flow slots in the top support plate and the bottom support plate were examined and found to have hourglassed significantly. A maximum slot displacement of 3.5 cm was noted on the bottom support plate. As a result, all of the tubes in row 1, approximately 2/3 of the tubes in row 2 and approximately 1/3 of the tubes in row 3 of each generator were plugged in October 1976 (Table 9.2).

Through 1976, 9.7% of the steam generator tubes had been plugged:

Steam Generator		Tubes Plugged	Percent of Total
A		312	9.2
B		315	9.3
C		362	10.7
	Total	989	9.7

Turkey Point 4: Turkey Point 4 steam generator inspection results are shown in Table 9.3. History at this plant was similar to that at Surry 2. Turkey Point 4 was given a nominal 100% baseline inspection prior to the June 1973 startup with inspection mostly to the first support plate. The

TABLE 9.3

EDDY CURRENT TUBE EXAMINATIONS

TURKEY POINT 4

(400 KHz)

		Tubes Probed				Eddy Current Signals >20%			
		Inlet		Outlet					
Date	SG	FS	UB	FS	UB	HL	CL	Tubes Plugged	Leaking Tubes
2/73	A					0	0	0	
	B	Nominal 100% Baseline				0	0	0	
	C					0	0	0	
1/74	A	61*	0	61*	0	0			
8/74	A	2005		442	0	127	6	34	1
	B	2116	0	0	46	174	0	43	
	C	2112	0	0	46	23	0	8	
9/74 Change to AVT chemistry									
5/75	A	2082	193	1426	46	124	194	63	
	B	1852	94	1107	138	129	216	66	
	C	710	271	1977	39	19	411	96	
8/75	B		39		39			1	1
9/75	B		115					11	1
1/76	C		49					2	1
4/76	A	Data unavailable						1	
	B							3	
	C							6	
9/76	B							3	
	C							6	1
9/76	B							34	4
10/76	B							4	2
11/76	A, B, C							All row 1	
	B							16	

FS = Through first support plate
UB = Around U-bend
HL = Hot leg
CL = Cold leg

*Run at 100 Khz

plant was shut down in August 1974 for a major steam generator inspection and water lancing prior to conversion to AVT. Some tube damage had occurred during operation with phosphate as indicated by the necessity to plug 85 tubes.

The first inspection after the change to AVT occurred in May 1975. At that time it appeared that the damage was continuing although 153 of the 225 tubes plugged had indications in the 40 to 49% range indicating they were plugged only because of the new 40% criteria. In August 1975, the plant was forced to shut down because of a primary to secondary leak in the B steam generator. The leak was found in a peripheral tube in a hard spot area (support plate section without flow holes). The leaker was probed and found to have a blockage (considered a dent) just below the second support plate preventing the passage of the U-bend probe (nominal 1.78 cm diameter). When probed from the cold leg through the U-bend, the probe only reached the sixth support plate in the hot leg side. Even a reduced diameter U-bend probe would not pass the obstruction in the second support. A similar problem was encountered with 38 other tubes in the same general vicinity. A review of the May 1975 inspection data by Westinghouse indicated that dents were present throughout the steam generator at that time.

Another shutdown was required in September 1975 because of a leaking tube, and again a large number of tubes were eddy current tested. All were found to contain denting with the worst obstructions being in the periperal tubes in the hard spot areas. In the April 1976 refueling outage, it was found that the damage from caustic attack or wastage as had been common previously apparently had been controlled. Only five tubes required plugging as a result of such attack. During the outage, a section of the sixth support plate was removed with tube segments as was done at Surry. Results of the Westinghouse examination were comparable to those at Surry.

Further leaks have been encountered as indicated in Table 9.3 with some of the leaks in the first row.

As a participant in an inspection program designed to investigate the cracking of small bend radius steam generator tubes as had occurred at Surry 2, Turkey Point 4 was shut down on October 28, 1976 for a steam generator inspection. Sections of 31 tubes (15 from row 1, 15 from row 2, and 1 from row 3) above the top support plate were removed from steam generator 4B. The tubes were adjacent to the outer top support plate flow slot. Tubes located near the center of the flow slot had a greater ovality than the tubes near the flow slot corners. Short longitudinal intergranular cracks 10 to 50% through the wall were found in three of the row 1 tubes located near the center of the flow slot.

Flow slot measurements taken in steam generator 4B indicated all six flow slots of the bottom support plate showed hourglassing whereas only three were noted on the top support plates. As a result, all tubes in row 1 of the three steam generators were plugged.

Sludge Deposits

One of the characteristics noted during the operation with phosphate chemistry was the buildup of a sludge deposit generally in the central region of the steam generator tube sheet. The stress cracking and wastage of the tubes encountered with phosphate chemistry occurred within this sludge blanket. An indication of the height of the sludge deposit was obtained by use of 25 KHz eddy current measurements. Measurements made by this method prior to the conversion to AVT indicated sludge piles as high as 7 to 10 cm in the hot leg and up to 17 cm in the cold leg of both Surry 2 and Turkey Point 4 steam generators. Measurements made before and after water lancing indicated no noticeable differences in eddy current measurement after the removal of the sludge by the water lancing. Despite water lancing at each major shutdown, the indicated height of the sludge pile after conversion to AVT has continued to increase. Although very little sludge buildup has been noted at the two Prairie Island units, a definite increase in indicated sludge height (maximum of 7.6 cm) and affected area relative to previous inspections was noted during the November

1976 Prairie Island 2 inspection. No sludge was noted on the tube sheet at Calvert Cliffs.

Discussion

Eddy current inspections have become an accepted method for indicating the presence and extent of caustic cracking or wastage of Alloy 600. Although the accuracy of the technique has at times been questioned, the general trend of the attack can be followed. With the advent of denting, the original eddy current inspection techniques were not adequate, and improved techniques had to be developed by the NSSS vendors. Such procedures currently are being employed to quantify the extent of this new type of attack at operating PWRs.

Section 10
PROGRAM PLANS

As a result of the observations made during the course of this program, recommendations for continued work in the area of PWR secondary chemistry were developed. The recommended efforts are intended to continue the general data collection activities on all aspects of PWR secondary system chemistry at the five study plants while focusing in several areas relatively recently identified as being of critical concern to the long term integrity of the steam generator systems. Each of the major areas of recommended effort are currently under negotiation with EPRI as discussed below.

Analytical Modeling

Solution chemistry variations with concentration both in the isolated cavity and equilibrium models developed in the original program should be studied relative to the effects of reactions of concentrated condenser leakage contaminants with metals and metal oxides. In particular, reactions of these solutions with magnetite, Alloy 600, and carbon steel should be considered. In addition, use of the model to determine the variations in solution chemistry which would be expected to result with variations in volatile pH control additive need to be evaluated.

General Chemistry

Collection, compilation, and review of general operating steam generator blowdown chemistry from each of the operating plants should be continued. This general chemistry follow will lead to continued knowledge of the effects of major system variations on steam generator chemistry. Without such an ongoing data compilation and evaluation effort, the environment leading to observed corrosion cannot be readily assessed.

Chloride Follow

Intensive studies at three operating plants to determine the variations in chloride concentrations in the condensate, feedwater, and steam generator blowdown during normal operation and periods of condenser leakage should be performed. The goal of the measurement program should be to understand chloride behavior particularly in the steam generator thereby allowing a clearer assessment of effects of chloride on steam generator materials corrosion. Recommended plants are Calvert Cliffs, Surry 2 or Turkey Point 4 and Prairie Island 1 or 2. Chloride analyses also should be performed on the moisture separator and heater drains to identify the degree of chloride exposure of turbine materials. The chloride follow will require development of low level chloride monitoring techniques. After initial intensive study programs of one to two weeks, continuous chloride concentration measuring devices should be installed on the steam generator blowdowns at two of the plants. This will allow long term variations in chloride concentration with variations in plant operating mode to be determined. Insight into the hideout and release mechanisms of chloride in the steam generators should be developed within the scope of this effort.

Hydrogen Follow

At least at one plant (preferably Surry 2 or Turkey Point 4), a hydrogen balance should be performed around the steam generator to determine the rate of hydrogen generation in a plant subject to accelerated denting. Subsequent to the short term intensive study of several weeks, hydrogen analysis equipment should be installed in the steam sample lines and then operated for approximately 6 months to determine the variation in hydrogen evolution which occurs as a function of plant operating mode. Efforts currently being performed by Westinghouse in this area should not be duplicated, i.e., attempts should be made to expand on the Westinghouse data base while making use of their current technology.

Oxygen Follow

At Prairie Island 1 or 2, Calvert Cliffs, and Surry 2 or Turkey Point 4, an intensive study of oxygen transport throughout the feedwater system should be performed. Subsequent to this study, an oxygen monitor should be installed on the steam generator blowdown at each of the three plants to allow data base expansion relative to the variation in oxygen concentrations with plant operating mode. Concurrently, data should be collected from plant installed oxygen monitoring equipment on feedwater and/or condensate.

Corrosion Product/Hardness Follow

Collection of corrosion product and hardness element transport data throughout the feedwater system including the steam generator blowdown should be continued at approximately 1/2 the level employed during the original program. Emphasis should be placed on defining differences in corrosion product and hardness element transport which occur with the use of condensate demineralizers. As such, efforts should be focused on Calvert Cliffs after routine operation of the powdered resin condensate treatment system begins. These data should be complemented by results from Prairie Island 1 and possibly Prairie Island 2 after the powdered resin filter demineralizer condensate treatment systems are put in service at these plants. In addition, effort should be made to augment the available data base on corrosion product and hardness transport throughout the system in the absence of condensate treatment.

Sludge Characterization

Several sludge samples from each plant should be analyzed by a variety of techniques. Such techniques should lead to the identification of all significant metallic and anionic species in the sludge. In particular, emphasis should be placed on possible failure related species such as lead, chloride, sulfate, etc. A cursory effort to define room temperature adsorptive properties of magnetite for sodium chloride also appears to be warranted.

Data Evaluation

The current level of data evaluation and interpretation of results obtained in the program should be expanded. In addition, efforts should be made to establish more extensive interchanges of data with NSSS vendors and other cognizant personnel in the industry. In particular, interfacing of activities performed in an extended program of the type described above with the Combustion Engineering model boiler test program has become mandatory.

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Appendix A

Development of Solution Chemistry Models

1. Introduction

As part of the work to determine the effects of coolant in-leakage on the water chemistry in steam generators, it is desirable to consider the variation in chemistry of solutions formed from steam generator bulk water as the steam quality is increased along the length of the generator, as well as of the residual solutions formed in cavities, e.g., in the pores of porous deposits from which liquid may evaporate. Such situations have been approximated by relatively simple models believed sufficient to establish chemistry trends at a reasonable confidence level.

Two models were developed: one, denoted as the "Dynamic Equilibrium Model", attempts to predict variations in chemistry of a solution initially in the liquid state at operating temperature, where the steam quality is increased from zero to near 100% at constant mass and constant temperature. The vapor phase is assumed to be in equilibrium with the liquid phase as the steam fraction is increased.

In the second model, denoted as the "Isolated Cavity Model", the vapor is allowed to escape as the liquid mass is reduced to near dryness. The chemistry of each differential amount of escaping vapor is assumed to be in equilibrium with the remaining liquid.

In both models, the liquid phase ionic residues are assumed to be in equilibrium with any solid precipitates. Resolubilization of precipitates can be allowed to reflect rapid dissolution kinetics. This assumption was made in the cases evaluated to date. Alternatively, resolubilization may be eliminated to reflect slow dissolution of previously formed precipitates.

There are only minor variations between the two models in the computational procedures. Basic to both models are the equilibrium equations relating dissolved species in the liquid residue to each other and to any solid phase precipitates which are formed.

The species considered in the modeling process are: water solvent, its ions H^+ and OH^-, NH_3, its cation NH_4^+, sulfate $SO_4^=$ and bisulfate HSO_4^- anions, carbon dioxide CO_2, its anions $CO_3^=$ and HCO_3^-, chloride Cl^-, sodium Na^+, calcium Ca^{++} and magnesium Mg^{++}. The possible precipitates are calcium sulfate $CaSO_4$, calcium hydroxide $Ca(OH)_2$ and magnesium hydroxide $Mg(OH)_2$.

It is necessary to distinguish eight possible situations:

1 - No precipitate
2 - Only $CaSO_4$ precipitates.
3 - Only $Ca(OH)_2$ precipitates.
4 - Only $Mg(OH)_2$ precipitates.
5 - $CaSO_4$ and $Ca(OH)_2$ precipitate but not $Mg(OH)_2$.
6 - $CaSO_4$ and $Mg(OH)_2$ precipitate but not $Ca(OH)_2$.
7 - $Ca(OH)_2$ and $Mg(OH)_2$ precipitate but not $CaSO_4$.
8 - $CaSO_4$, $Ca(OH)_2$ and $Mg(OH)_2$ precipitate.

For each case, a different set of relations, which are solved simultaneously by iteration,applies.

Various iterative procedures can be applied with different degrees of success in convergence. A modified Newton-Raphson procedure was found to yield reasonable convergence for all initial solution compositions and for all residual solutions resulting from the concentrating processes encountered to date. There is no assurance that the same success will be obtained with other solution compositions. In cases where the procedures fail to yield convergence, it would be necessary to vary the mathematical procedures or to displace the value of the concentration factor considered.

In Section 2, general relations are given. In the following sections, the eight precipitation modes are treated, in the order listed above.

The criteria used to determine which set of equations applies to a given residual solution (before pH is known) are incorporated within the iteration loops. The criteria are established in Section 11. The iteration scheme also is discussed in the same section.

Treatment of the volatile species, which is dependent on the model chosen (dynamic equilibrium or isolated cavity), is considered in Section 12.

The computer programs for the two models, with resolubilization being allowed, are appended at the end of section 12.

2. Nomenclature and General Relations

A detailed nomenclature is given in the list of symbols at the end of this appendix. In the following discussion, 0, B1, S1, S2, H1, L1, N, C and M represent the concentrations in solution of ions OH^-, NH_4^+, $SO_4^=$, HCO_3^-, Cl^-, Na^+, Ca^{++}, and Mg^{++}, respectively. Because the carbonate species disappear very early in the process by volatilization of carbon dioxide when the solution pH is close to neutral, the concentration of $CO_3^=$ is negligible.

X1, X2 and X3 represent the amounts, if any, of precipitates $CaSO_4$, $Ca(OH)_2$ and $Mg(OH)_2$ respectively, in mole per kg of solution (from which it precipitates out). The variations of solution density with composition are neglected.

SO represents the total amount of bisulfate and sulfate including the amount in the $CaSO_4$ precipitated, CO the total amount of calcium including the amount in the $CaSO_4$ and the $Ca(OH)_2$ precipitated, and finally MO the total amount of magnesium including the amount in the $Mg(OH)_2$ precipitated.

The mass conservation relations for calcium, sulfur, and magnesium are as follows:

$$C + X1 + X2 = CO \qquad (2\text{-}1)$$

$$S1 + S2 + X1 = SO \qquad (2\text{-}2)$$

and $$M + X3 = MO \qquad (2\text{-}3)$$

Solubility products, when applicable, can yield up to three equations:

$$C * S2 = K6 \tag{2-4}$$

$$C * \emptyset^2 = K4 \tag{2-5}$$

$$M * \emptyset^2 = K3 \tag{2-6}$$

The sulfate-bisulfate equilibrium can be expressed as:

$$SO_4^{=} + H_2O \rightleftharpoons HSO_4^{-} + OH^{-} \tag{2-7}$$

for which the equilibrium constant is written as:

$$\frac{\emptyset * S1}{S2} = K5 \tag{2-8}$$

The ionic product for water is:

$$[H^+] * \emptyset = K1$$

from which

$$[H^+] = K1/\emptyset \tag{2-9}$$

The solution electroneutrality condition yields:

$$A + (2 * C) + (2 * M) + \frac{K1}{\emptyset} - \emptyset - 2\ (S1 + S2) + S1 = 0 \tag{2-10}$$

where A is defined as:

$$A \equiv N + B1 - L1 - H1 \tag{2-11}$$

Table A.1 lists pertinent equilibrium constants as functions of temperature and ionic strength.

3. Case (1), No Precipitate

In the case of no precipitation, equations (2-4, 5 and 6) are inapplicable. Instead, the following inequalities apply:

$$C * S2 < K6 \tag{3-1}$$

$$C * \emptyset^2 < K4 \tag{3-2}$$

and

$$M * \emptyset^2 < K3 \tag{3-3}$$

TABLE A.1

PHYSICAL CHEMISTRY RELATIONS*

$H_2O \rightleftharpoons H^+ + OH^-$

$$\log Q = -\frac{151.713}{T} - 111.491 - 0.03685T + 44.077 \log T + \frac{5.36\sqrt{I}}{1+\sqrt{I}} - (0.6356 - 0.001078T)\, I$$

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$\log Q = -6.17 + \frac{2.396\sqrt{I}}{1+1.5\sqrt{I}} \qquad \text{(at 275°C)}$$

$Ca(OH)_2 \rightleftharpoons Ca^{++} + 2OH^-$

$$\log K_s = -25.7085 + 12.9722 \log T - \frac{530.49}{T} - 0.032331\,T + \frac{7.722\sqrt{I}}{1+2.16\sqrt{I}} - 0.16\,I + 0.0125\,I^2$$

$Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$

$$\log K_s = \log K_{s_{Ca(OH)_2}} - 5.6$$

$HSO_4^- \rightleftharpoons H^+ + SO_4^=$

$$\log Q = 91.471 - 33.0024 \log T - \frac{3520.3}{T} + \frac{4.792\sqrt{I}}{1+1.76\sqrt{I}}$$

$CaSO_4 \rightleftharpoons Ca^{++} + SO_4^=$

$$\log K_s = -133.207 + 53.5472 \log T + \frac{3569.6}{T} - 0.0529025\,T + \frac{9.584\sqrt{I}}{1+1.5\sqrt{I}}$$

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$$-\log K = \frac{2382.2}{T} - 8.153 + 0.02194\,T$$

Where K_s = Solubility product

K = Equilibrium constant

Q = Molal product

I = Ionic strength, Molality

T = Temperature, °K

* Carbonic acid data from Reference 10; Remaining relations from Reference 11

Also,

$$X1 = X2 = X3 = 0 \qquad (3\text{-}4)$$

Substituting these values in equations (2-1, 2 and 3):

$$C = CO \qquad (3\text{-}5)$$

$$S1 + S2 = SO \qquad (3\text{-}6)$$

$$M = MO \qquad (3\text{-}7)$$

Equation (2-8) and the electroneutrality equation (2-10) are valid for all cases. From equation (3-6):

$$S1 = SO - S2 \qquad (3\text{-}8)$$

Substituting into equation (2-8):

$$\frac{\phi * (SO - S2)}{S2} = K5$$

from which

$$S2 = \frac{SO}{1 + (K5/\phi)} = \frac{\phi * SO}{\phi + K5} \qquad (3\text{-}9)$$

Substituting into equation (3-8):

$$S1 = SO - S2 = \frac{K5 * SO}{\phi + K5} \qquad (3\text{-}10)$$

Substituting for C, M, (S1 + S2) and S1 from equation (3-5), (3-7), (3-6) and (3-10), respectively, into the electroneutrality equation (2-10) yields:

$$A + 2 * (CO + MO - SO) + \frac{K1}{\phi} - \phi + \frac{K5 * SO}{\phi + K5} = 0 \qquad (3\text{-}11)$$

This yields a third degree equation for ϕ:

$$\phi^3 + [K5 - A - 2 * (CO + MO - SO)] * \phi^2 + [So - 2 * (CO + MO) - A] * \phi - K1\ K5 = 0 \qquad (3\text{-}12)$$

Solution of equation (3-12) yields the value for ϕ. The pH of the solution is then:

$$P1 = -\log (K1/\phi) \qquad (3\text{-}13)$$

4. Case (2), Calcium Sulfate Precipitation

In the situation where only calcium sulfate precipitates, equations (2-5) and

(2-6) are inapplicable. Instead, inequalities (3-2) and (3-3) apply. Also,

$$X2 = X3 = 0 \qquad (4\text{-}1)$$

and substituting these values in equations (2-1) and (2-3):

$$C + X1 = CO \qquad (4\text{-}2)$$

$$M = MO \qquad (4\text{-}3)$$

Equations (2-2) and (2-4) remain valid in the present case. As previously noted, equations (2-8) and the electroneutrality equation (2-10) remain valid in all cases.

Eliminating X1 between equations (2-2) and (4-2) yields:

$$S1 + S2 = SO - CO + C \qquad (4\text{-}4)$$

From equation (2-4) and (2-8) respectively:

$$S2 = K6/C \qquad (4\text{-}5)$$

and $S1 = \frac{K5}{\emptyset} * S2 = \frac{K5 * K6}{\emptyset * C}$ (4-6)

Substituting into the electroneutrality equation (2-10) for M, (S1 + S2) and S1, from equations (4-3), (4-4), and (4-6), respectively, yields:

$$A + 2 * (CO + MO - SO) + \frac{K1}{\emptyset} - \emptyset + \frac{K5 * K6}{\emptyset * C} = 0 \qquad (4\text{-}7)$$

A second equation between the two unknowns C and $\emptyset$ is obtained by substituting for S2 and S1 from equations (4-5) and (4-6), respectively, into equation (4-4):

$$C^2 + (SO - C) * C - \left(1 + \frac{K5}{\emptyset}\right) * K6 = 0 \qquad (4\text{-}8)$$

Simultaneous solution of equations (4-7) and (4-8) yields the values for C and/or $\emptyset$. The pH is then expressed by equation (3-13).

5. Case (3), Calcium Hydroxide Precipitation

With only calcium hydroxide precipitation, equations (2-4) and (2-6) are inapplicable. Instead, inequalities (3-1) and (3-3) apply. Also,

$$X1 = X3 = 0 \tag{5-1}$$

and substituting these values in equations (2-1, 2 and 3):

$$C + X2 = CO \tag{5-2}$$

$$S1 + S2 = SO \tag{5-3}$$

$$M = MO \tag{5-4}$$

Equation (2-5) is valid in the present case. Equation (2-8) and the electroneutrality equation (2-10), remain valid.

Eliminating S2 between equations (2-8) and (5-3):

$$S1 = \frac{K5 * SO}{K5 + \phi} \tag{5-5}$$

Substitution in the electroneutrality equation (2-10), for M, (S1 + S2) and S1 from equations (5-4), (5-3) and (5-5), respectively, yields:

$$A + 2 * C + 2 * (MO - SO) + \frac{K1}{\phi} - \phi + \frac{K5 * SO}{K5 + \phi} = 0 \tag{5-6}$$

Simultaneous solution of equations (2-5) and (5-6) yields values for C and/or ϕ. The pH is then expressed by equation (3-13).

6. Case (4), Magnesium Hydroxide Precipitation

This case is symmetrical with case (3). The same equations are obtained with exchange of X3, M, MO and K3 with X2, C, CO and K4, respectively:

$$X1 = X2 = 0 \tag{6-1}$$

$$M + X3 = MO \tag{6-2}$$

$$S1 + S2 = SO \tag{6-3}$$

$$C = CO \tag{6-4}$$

$$S1 = \frac{K5 * \phi}{K5 + \phi} \tag{6-5}$$

$$A + 2 * M + 2 * (CO - SO) + \frac{K1}{\phi} - \phi + \frac{K5 * SO}{K5 + \phi} = 0 \tag{6-6}$$

Equations (2-4) and (2-5) are inapplicable. Instead, inequalities (3-1) and (3-2) apply. Equation (2-6) is valid.

Simultaneous solution of equations (2-6) and (6-6) yields values for M and/or ϕ. The pH is then expressed by equation (3-13).

7. Case (5), Calcium Sulfate and Calcium Hydroxide Precipitation

In this case, equation (2-6) is inapplicable. Instead, inequality (3-3) applies. Also,

$$X3 = 0 \tag{7-1}$$

and substituting this value in equation (2-3):

$$M = MO \tag{7-2}$$

Equations (2-1), (2-2), (2-4), and (2-5) are valid in the present case. Equation (2-8) and the electroneutrality equation (2-10) remain valid.

From equations (2-4) and (2-8), respectively:

$$S2 = K6/C \tag{7-3}$$

and $$S1 = \frac{K5}{\phi} * S2 = \frac{K5 * K6}{\phi * C} \tag{7-4}$$

Substitution into the electroneutrality equation (2-10), for M, S2 and S1 from equations (7-2), (7-3) and (7-4), respectively, yields:

$$A + (2 * C) + (2 * MO) + \frac{K1}{\phi} - \phi - (2 + \frac{K5}{\phi}) * \frac{K6}{C} = 0 \tag{7-5}$$

Simultaneous solution of equations (2-5) and (7-5) yields values for C and/or ϕ. The pH is expressed by equation (3-13).

8. Case (6), Calcium Sulfate and Magnesium Hydroxide Precipitation

In this case, equation (2-5) is inapplicable. Instead, inequality (3-2) applies. Also,

$$X2 = 0 \tag{8-1}$$

and substituting this value in equation (2-1):

$$C + X1 = CO \tag{8-2}$$

Equations (2-2), (2-3), (2-4) and (2-6) are valid in the present case. Equation (2-8) and the electroneutrality equation (2-10) are valid.

Eliminating X1 between equations (2-2) and (8-2), yields:

$$S1 + S2 = SO - CO + C \tag{8-3}$$

From equations (2-4) and (2-8), respectively:

$$S2 = K6/C \tag{8-4}$$

and

$$S1 = \frac{K5}{\phi} * S2 = \frac{K5 * K6}{\phi * C} \tag{8-5}$$

Substitution of these expressions into equation (8-3), yields:

$$C^2 + (SO - CO) * C - (1 + \frac{K5}{\phi}) * K6 = 0 \tag{8-6}$$

A second relation between the two unknowns C and ϕ is obtained by substitution into the electroneutrality equation (2-10) for M, (S1 + S2) and S1 from equations (2-6), (8-3), and (8-5), respectively:

$$A + (2 * \frac{K3}{\phi^2}) + \frac{K1}{\phi} - \phi - 2 * (SO - CO) + \frac{K5 * K6}{\phi * C} = 0 \tag{8-7}$$

Simultaneous solution of equations (8-6) and (8-7) yields the values for C and/or ϕ. The pH is given by equation (3-13).

9. Case (7), Calcium and Magnesium Hydroxide Precipitation

In this case, equation (2-4) is inapplicable. Instead, inequality (3-1) applies. Also,

$$X1 = 0 \tag{9-1}$$

and substituting this value in equations (2-1) and (2-2):

$$C + X2 = CO \tag{9-2}$$

$$S1 + S2 = SO \tag{9-3}$$

Equations (2-3), (2-5) and (2-6) are valid in the present case. Equation (2-8) and the electroneutrality equation (2-10) remain valid.

Eliminating ϕ between equations (2-5) and (2-6) yields:

$$M = \frac{K3}{K4} * C \qquad (9\text{-}4)$$

Eliminating S2 between equations (2-8) and (9-3) yields:

$$S1 = \frac{K5 * SO}{K5 + \phi} \qquad (9\text{-}5)$$

From equation (2-5):

$$\phi = \frac{\sqrt{K4}}{\sqrt{C}} \qquad (9\text{-}6)$$

and substitution into equation (9-5):

$$S1 + \frac{K5 * SO}{K5 + \frac{\sqrt{K4}}{\sqrt{C}}} = \frac{K5 * SO * \sqrt{C}}{K4 + K5 \quad \sqrt{C}} \qquad (9\text{-}7)$$

Substitution into the electroneutrality equation (2-10), for (S1 + S2), M, ϕ and S1, from equations (9-3), (9-4), (9-6) and (9-7), respectively, yields:

$$2 * (1 + \frac{K3}{K4}) * K5 * Y^4 + (2 * K4 + K3 + \frac{K1 * K5}{\sqrt{K4}}) * Y^3 + (K1 * \sqrt{K4} + A - SO) * Y^2 + (A - 2 * SO - \frac{K5}{\sqrt{K4}}) * K4 * Y - K4 * \sqrt{K4} = 0 \qquad (9\text{-}8)$$

where Y is defined as:

$$Y = \sqrt{C} \qquad (9\text{-}9)$$

Solution of equation (9-8) and substitution into (9-9) and then into (9-7) yields the value of ϕ. The pH is given by equation (3-13).

10. Case (8), Calcium Sulfate, Calcium Hydroxide and Magnesium Hydroxide Precipitation

In this case, all the equations in Section 2 are valid.

Elimination of ϕ between equations (2-5) and (2-6) yields:

$$M = \frac{K3}{K4} * C \qquad (10\text{-}1)$$

From equation (2-4):

$$S2 = \frac{K6}{C} \qquad (10\text{-}2)$$

From equation (2-5):

$$\emptyset = \frac{\sqrt{K4}}{\sqrt{C}} \qquad (10\text{-}3)$$

From equation (2-8):

$$S1 = \frac{K5}{\emptyset} * S2 \qquad (10\text{-}4)$$

Substitution for S2 from equation (10-2) and for Ø from equation (10-3) yields:

$$S1 = \frac{K5 * K6}{\sqrt{K4} * \sqrt{C}} \qquad (10\text{-}5)$$

Substitution into the electroneutrality equation (2-10) for M, S2, Ø and S1 from equations (10-1), (10-2), (10-3) and (10-5), respectively, yields:

$$2 * \left(1 + \frac{K3}{K4}\right) * Y^4 + \frac{K1}{\sqrt{K4}} * Y^3 + A * Y^2 - \frac{K4 - K5 * K6}{\sqrt{K4}} * Y - 2 * K6 = 0 \qquad (10\text{-}6)$$

where Y is defined by equation (9-9).

Solution of equation (10-6) and substitution into equation (9-9) and then into equation (10-3) yield the value for Ø. The pH is expressed by equation (3-13).

11. Determination of the Relevant Set of Equations

Calcium sulfate will not precipitate as long as the ionic product CO * S2 is smaller than the solubility product K6, i.e.:

$$CO * S2 < K6 \qquad (11\text{-}1)$$

Similarly for calcium and magnesium hydroxides:

$$CO * \emptyset^2 < K4 \qquad (11\text{-}2)$$

$$MO * \emptyset^2 < K3 \qquad (11\text{-}3)$$

If ϕ and S2 were known, (11-1), (11-2), and (11-3) would make suitable criteria. Inequality (11-1) can be cast in a more suitable form by recalling that equation (2-8) is valid for all cases and therefore can be applied to express S1 as:

$$S1 = \frac{K5}{\phi} * S2$$

and adding S2 on both sides:

$$S1 + S2 = (1 + \frac{K5}{\phi}) * S2$$

from which

$$S2 = \frac{S1 + S2}{1 + \frac{K5}{\phi}} \qquad (11\text{-}4)$$

Substitution of this expression for S2 into inequality (11-1) and rearrangement, yield:

$$CO * (S1 + S2) < K6 * (1 + \frac{K5}{\phi}) \qquad (11\text{-}5)$$

Moreover, as long as calcium sulfate is not precipitating, then

$$X1 = 0 \qquad (11\text{-}6)$$

equation (2-2) becomes

$$S1 + S2 = SO \qquad (11\text{-}7)$$

and this expression can be substituted into inequality (11-5) to yield:

$$CO * SO < K6 * (1 + \frac{K5}{\phi}) \qquad (11\text{-}8)$$

Inequality (11-3) is a necessary and sufficient condition for non-precipitation of magnesium hydroxide. Inequalities (11-2 and 8) are independently sufficient <u>but not necessary</u> conditions for non-precipitation of calcium hydroxide and calcium sulfate, respectively. That is if either of (11-2) or (11-8) (or both) is satisfied, the test is conclusive; if neither is met, additional testing is required. These additional tests are derived by considering that when the calcium ion is in equilibrium with both its hydroxide and its sulfate, the following relations must apply:

$$C = \frac{K4}{\phi^2} \qquad (11\text{-}9)$$

and $$\frac{SO}{1 + K5/\phi} > S2 = \frac{K6}{C}$$

from which:

$$SO * C > K6 * (1 + \frac{K5}{\phi}) \tag{11-10}$$

and substituting for C from equation (11-9):

$$\frac{SO * K4}{\phi^2} > K6 * (1 + \frac{K5}{\phi}) \tag{11-11}$$

If neither of the three inequalities (11-2, 8 and 11) is met, calcium hydroxide precipitates, but not calcium sulfate.

If only inequalities (11-2 and 8) are not met, but (11-11) is verified, calcium sulfate precipitates and one more test is required for calcium hydroxide. For this purpose, the would be calcium concentration in absence of calcium hydroxide precipitation, is calculated from equation (4-8), or from (8-6) which is identical to (4-8), and the ionic product is compared to the solubility product. If

$$C * \phi^2 > K4 \tag{11-12}$$

the hydroxide precipitates with the sulfate, if not, calcium hydroxide does not precipitate.

The problem now is to determine initially the correct value of ϕ. Various procedures are possible. The procedure used in this work is, in principle, as follows:

1 - A tentative value $\phi 1$ is guessed for ϕ. For an initial solution (before concentrating) $\phi 1$ corresponds to neutral pH at operating temperature. For a residual solution, the last pH value yields the tentative guess for $\phi 1$.

2 - The criteria are used to determine which species would precipitate, i.e, which one of the eight sets of equations applies.

3 - The equations are solved and ϕ determined.

4 - The value ϕ is compared to the value $\phi 1$. If close enough (within a

preselected accuracy limit), the case was solved correctly and the value calculated for Ø is its correct value. If the values Ø and Ø1 are not close enough, the previous guess Ø1 is discarded and the value of Ø is assigned to Ø1 as a better guess to repeat the procedure from step (2), and so on until Ø ∿ Ø1.

This procedure allows updating the values of the ionic strength and of the solubility porducts and other equilibrium constants, at each computational cycle, when the necessary data are available.

In general, the procedure converges because the validity of each of the eight sets of equations covers a wide range of Ø values.

12. Volatiles

The ions produced by the reversible dissociation of volatile species are removed from the solution in the early stages of the concentrating process, before conditions for participating in the formation of precipitates can be reached. However, during these early stages, these ionic species affect the pH of the solution.

The volatile species considered in this work are carbon dioxide and ammonia, or morpholine or cyclohexylamine. Only ammonia is discussed below.

Ammonia reacts with water to form ammonium hydroxide in equilibrium with the ions formed by dissociation:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \qquad (12\text{-}1)$$

Letting B and B1 represent the concentrations of NH_4OH and NH_4^+, respectively, in solution, the equilibrium constant for the reaction (12-1) is defined as

$$\frac{B1 * \emptyset}{B} = K2 \qquad (12\text{-}2)$$

Define also:

$$\frac{B}{B + B1} \equiv F2 \qquad (12\text{-}3)$$

From equation (12-2):

$$\frac{B1}{B} = \frac{K2}{\emptyset}$$

and

$$\frac{B + B1}{B} = 1 + \frac{B1}{B} = 1 + \frac{K2}{\emptyset} = \frac{\emptyset + K2}{\emptyset}$$

from which

$$F2 \equiv \frac{B}{B + B1} = \frac{\emptyset}{\emptyset + K2} \qquad (12\text{-}4)$$

The distribution coefficient for ammonia is defined as:

$$D2 = \frac{\text{molal concentration of } NH_3 \text{ in vapor phase}}{\text{molal concentration of } NH_4OH \text{ in liquid phase}} \qquad (12\text{-}5)$$

Whether ammonia in the vapor mixture is hydrated or not is irrelevant here. To pursue the treatment, the model selected must now be specified.

Dynamic Equilibrium Model:

Consider an initial liquid mass L° with total ammonia concentration BO, i.e.:

$$BO = B^\circ + B1^\circ \qquad (12\text{-}6)$$

where B° and B1° are the initial concentrations of NH_4OH and NH_4^+, respectively, in the initial liquid mass L°. Let L and V represent the masses in the liquid and vapor phases.

A mass balance over the system yields:

$$L + V = L^\circ \qquad (12\text{-}7)$$

Conservation of the ammonia species yields:

$$(B1 + B)L + D2 * B * V = BO * L^\circ$$

Substitution for B and for V from equations (12-3) and (12-7), respectively, yields:

$$(B1 + B) * [L + D2 * F2 * (L^\circ - L)] = BO * L^\circ$$

from which:

$$B1 + B = \frac{BO * L^\circ}{L + D2 * F2 * (L^\circ - L)}$$

or

$$B1 + B = \frac{BO}{\frac{L}{L^\circ} + (1 - \frac{L}{L^\circ}) * D2 * F2} \qquad (12\text{-}8)$$

Defining a concentration factor as:

$$T1 = \frac{L^\circ}{L} \qquad (12\text{-}9)$$

and substituting into equation (12-8) yields:

$$B1 + B = \frac{BO}{\frac{1}{T1} + (1 - \frac{1}{T1}) * D2 * F2} \quad (12\text{-}10)$$

From equation (12-3):

$$B = F2 * (B + B1)$$

so that

$$B1 \equiv (B + B1) - B = (1 - F2)\ (B + B1) \quad (12\text{-}11)$$

and substituting for (B + B1) from equation (12-10):

$$B1 = \frac{(1 - F2) * BO}{\frac{1}{T1} + (1 - \frac{1}{T1}) * D2 * F2} \quad (12\text{-}12)$$

Similarly for carbon dioxide:

$$H1 = \frac{(1 - F7) * HO}{\frac{1}{T1} + (1 - \frac{1}{T1}) * D7 * F7} \quad (12\text{-}13)$$

where H1 represent the concentration of bicarbonate ion HCO_3^- in the liquid phase, HO the conserved total amount of CO_2 in its various forms in the two phases, D7 is the partition coefficient for CO_2:

$$D7 \equiv \frac{\text{molal concentration of } CO_2 \text{ in the vapor phase}}{\text{molal concentration of } H_2CO_3 \text{ in the liquid phase}} \quad (12\text{-}14)$$

and

$$F7 \equiv \frac{(H_2CO_3)}{(H_2CO_3) + (HCO_3^-)} = \frac{K7}{K7 + \emptyset} \quad (12\text{-}15)$$

where K7 is the equilibrium constant

$$K7 = \frac{(H_2CO_3) * \emptyset}{HCO_3^-} \quad (12\text{-}16)$$

for the equilibrium:

$$HCO_3^- + H_2O \rightleftarrows H_2CO_3 + OH^- \quad (12\text{-}17)$$

The second dissociation equilibrium

$$CO_3^= + H_2O \rightleftarrows HCO_3^- + OH^- \quad (12\text{-}18)$$

is neglected because practically all the carbon dioxide escapes very early in the concentrating process before the pH can change sufficiently to make the concentration of $CO_3^=$ appreciable.

Equations (12-12) and (12-13) determine the ionic contributions of ammonia and of carbon dioxide, respectively, in the liquid residue as the steam quality of the constant mass is increased at constant temperature and pressure.

Isolated Cavity Model

Consider a differential mass dL escaping from a residual liquid mass L with molal concentrations B1 and B of NH_4^+ and NH_4OH, respectively.

The concentration of ammonia in dL is (D2 * B) and the number of moles of ammonia escaping in dL is then:

$$d[(B + B1) * L] = D2 * B * dL \qquad (12\text{-}19)$$

but

$$d[(B + B1) * L] = (B + B1) * dL + L * d(B + B1) \qquad (12\text{-}20)$$

Comparison with equation (12-19) yields:

$$[(D2 * B) - (B + B1)]dL = L * d(B + B1)$$

and substituting for B in the first term on the left side, from equation (12-3):

$$(D2 * F2 - 1)\ (B + B1) * dL = L * d(B + B1)$$

or

$$\frac{1}{D2 * F2 - 1} * \frac{d(B + B1)}{B + B1} = \frac{dL}{L} \qquad (12\text{-}21)$$

From equation (12-4) it is seen that F2 is a function of pH and of K2, and both these are functions of the total composition. Nevertheless, equation (12-21) may be solved by integrating on both sides over a small range for which F2 does not vary appreciably, yielding:

$$\text{Log}\ \frac{(B + B1)_{n+1}}{(B + B1)_n} = (D2 * F2 - 1) * \text{Log}\ \frac{L_{n+1}}{L_n}$$

or

$$(B + B1)_{n+1} = (B + B1)_n \left(\frac{T1_n}{T1_{n+1}}\right)^{(D2 * F2 - 1)}$$

and since F2 has not varied appreciably over the small range from $T1_n$ to $T1_{n+1}$,

$$B1_{n+1} = B1_n \left(\frac{T1_n}{T1_{n+1}}\right)^{(D2 * F2 - 1)} \qquad (12\text{-}22)$$

Alternatively, for such a small step, equation (12-21) can be cast in the form of a difference equation:

$$\frac{(B + B1)_{n+1} - (B + B1)_n}{(B + B1)_n} = (D2 * F2 - 1) * \frac{L_{n+1} - L_n}{L_n}$$

or

$$\frac{(B + B1)_{n+1}}{(B + B1)_n} = 1 + (D2 * F2 - 1) * \left(\frac{T1_n}{T1_{n+1}} - 1\right)$$

and since the ratio F2 (see equation 12-3) has not changed appreciably:

$$(B1)_{n+1} = (B1)_n * \{1 - (D2 * F2 - 1) * [1 - \frac{(T1)_n}{(T1)_{n+1}}]\} \qquad (12\text{-}23)$$

Equation (12-21) can be solved over a wide range by using either of equations (12-22) or (12-23) over successive small steps and updating the value of F2 by determining the chemistry of the residual solution after each small incremental step.

Similarly for carbon dioxide with the following two equations:

$$H1_{n+1} = H1_n \left(\frac{T1_n}{T1_{n+1}}\right)^{(D7 * F7 - 1)} \qquad (12\text{-}24)$$

$$H1_{n+1} = H1_n * \{ 1 - (D7 * F7 - 1) * [1 - \frac{T1_n}{T1_{n+1}}] \} \qquad (12\text{-}25$$

corresponding to equations (12-22) and (12-23), respectively.

LIST OF SYMBOLS

A	An algebraic sum defined by equation (2-11).
B	Concentration of neutral species NH_4OH in the liquid, mole/Kg.
B1	Concentration of cation NH_4^+ in the liquid, mole/Kg.
B°, B1°	Initial values (before concentrating) of B and B1, respectively, mole/Kg.
BO	($\equiv B° + B1°$), mole/Kg.
C	Concentration of calcium ion Ca^{++} in the liquid, mole/Kg.
CO	Total calcium in residue (liquid + precipitate), mole/Kg.
D2	Vapor/liquid partition coefficient for ammonia.
D7	Vapor/liquid partition coefficient for carbon dioxide.
F2	Fraction of undissociated ammonia in the liquid [$\equiv NH_4OH/(NH_4OH + NH_4^+)$].
F7	Fraction of undissociated carbonic acid in the liquid [$\equiv H_2CO_3/(H_2CO_3 + HCO_3^-)$].
H1	Concentration of bicarbonate anion HCO_3^- in the liquid, mole/Kg.
HO	Initial concentration (before evaporating) of total carbon dioxide ($H_2CO_3 + HCO_3^-$) in the liquid, mole/Kg.
I	Ionic strength, (mole equivalent)^2/mole.
I1	Tentative value of ionic strength, (mole equivalent)^2/mole.
K1	Ionic product for water, (mole/Kg)^2.
K2	Equilibrium constant for ammonia dissociation in aqueous solutions, mole/Kg.
K3	Solubility product for magnesium hydroxide, (mole/Kg)^3.
K4	Solubility product for calcium hydroxide, (mole/Kg)^3.
K5	Sulfate/bisulfate equilibrium constant defined by equation (2-8), mole/Kg.
K6	Solubility product for calcium sulfate, (mole/Kg)^2.
K7	Equilibrium constant for first dissociation of carbonic acid in aqueous solutions, mole/Kg.
L	Mass of the liquid, Kg.
L°	Initial mass of the liquid, Kg.
L1	Concentration of chloride ion Cl^- in the liquid, mole/Kg.

Concentration of magnesium ion Mg^{++} in the liquid, mole/Kg.

Total magnesium in residue (liquid + precipitate), mole/Kg.

Concentration of sodium ion Na^{+} in the liquid, mole/Kg.

Concentration of hydroxyl ion OH^{-} in the liquid, mole/Kg.

pH of liquid.

Concentration of bisulfate ion HSO_4^{-} in the liquid, mole/Kg.

Concentration of sulfate ion $SO_4^{=}$ in the liquid, mole/Kg.

Total sulfur (bisulfate + sulfate in liquid and in precipitate) in residue, mole/Kg.

Concentration factor ($\equiv L^\circ/L$).

Mass of vapor, Kg.

Precipitated calcium sulfate in residue, mole/Kg.

Precipitated calcium hydroxide in residue, mole/Kg.

Precipitated magnesium hydroxide in residue, mole/Kg.

DYNAMIC EQUILIBRIUM MODEL

```
1 :##.#-#.#!!!!-#.###!!!!-#.###!!!!-#.###!!!!-#.###!!!!-#.!!!!

3 :##.#-#.#!!!!-#.###!!!!-#.###!!!!-#.###!!!!-#.###!!!! ##.###

5 E8=0.0023
10 E9=1.E-11
15 DEF FNI(O)=2*(C+M+S2)+(N+L1+S1+K1/O+O+H1+B1)/2
52 DEF FNX(O)=S1*(S1/(C+S1+S2)-1)/O
54 DEF FNY(O)=(-1-K1/O/O)
130 :S.Q.  [H]      [OH]       [CA]       [MG]       [SO4]      [HSO4]    Z/E

140 :S.Q. [AMINE]T [AMINE]+  [CO2]T     [HCO3]     [CATIONS] [ANIONS]   PH

150 :################### WITH ###################
160 T=273+280
170 D7=800
180 OPEN 1,'FILE9',OUTPUT
190 OPEN 5,'FILE5',OUTPUT
200 Q1=10↑(-151.713/T-111.491-.03685*T+44.077*LGT(T))
210 Q4=10↑(-25.7085+12.9722*LGT(T)-530.49/T-.032331*T)
220 Q3=Q4*10↑(-5.6)
230 Q5=10↑(91.471-33.0024*LGT(T)-3520.3/T)
240 Q6=10↑(-133.207+53.5472*LGT(T)+3569.6/T-.0529025*T)
250 Q7=10↑(-2382.2/T+8.153-.02194*T)
260 REM READ K AMINE,VAP/LIQ RATIO,CONC.,NAME
270 DATA 6.7608E-7,3.7,1.45E-5
280 READ Q2 ,D2,B0
290 A$='AMMONIA'
300 REM READ NA,CL,MG,CA,S4,HCO3
310 DATA 1.73E-04,1.97E-04,1.93E-05,3.67E-06,1.01E-05,2.41E-06,1.45E-5
320 READ N9,L0,M9,C9,S9,H0
330 B$='SEA WATER'
340 PUT 5:B$,A$
350 REM INITIALIZING
360 T0=1
370 N0=N9*T0
380 L1=L0*T0
390 M0=M9*T0
400 C0=C9*T0
405 S0=S9*T0
406 N=N0
410 M=M0
420 C=C0
430 S1=S0
440 O=SQR(Q1)
```

```
450 PRINT USING 150,B$,A$
460 PRINT
470 PRINT USING 130
480 I=FNI(O)
490 GOSUB 510
500 GO TO 600
510 REM TO REDEFINE K'S
520 K1=Q1*10↑(5.36*SQR(I)/(1+SQR(I))-(.6356-.001078*T)*I)
530 K2=Q2*10↑(2.396*SQR(I)/(1+1.5*SQR(I)))
540 K4=Q4*10↑(7.722*SQR(I)/(1+2.16*SQR(I))-.16*I+.0125*I↑2)
550 K3=K4*10↑(-5.6)
560 K5=K1/(Q5*10↑(4.792*SQR(I)/(1+1.76*SQR(I))))
570 K6=Q6*10↑(9.584*SQR(I)/(1+1.51*SQR(I)))
580 K7=K1/Q7
590 RETURN
600 FOR T3=1 TO 5
605 T0=10↑(T3-1)
607 T1=100-100/T0
610 REM SOLUTION CONTENTS PER KG.
620 N=N9*T0
630 L1=L0*T0
640 M0=M9*T0
650 C0=C9*T0
660 S0=S9*T0
700 U=1
720 GOSUB 510
730 GOSUB 750
740 GO TO 815
750 F2=O/(K2+O)
760 F7=K7/(K7+O)
770 B=B0/(1/T0+(1-1/T0)*F2*D2)
780 H=H0/(1/T0+(1-1/T0)*F7*D7)
790 B1=(1-F2)*B
800 H1=(1-F7)*H
810 RETURN
815 REM
820 IF M0*O*O>K3 THEN 2600
830 IF C0*O*O>K4 THEN 1700
840 IF C0*S0>K6*(1+K5/O) THEN 1300
850 REM NO PPT
860 M=M0
870 C=C0
880 O1=O
890 P0=1
900 FOR V=1 TO 20
910 S1=S0/(1+O/K5)
920 S2=S0/(1+K5/O)
930 GOSUB 5700     !TO CALCULATE  Z  AND TO TEST ACCURACY
932 IF P9=1 THEN 5410
935 IF P9=2 THEN 815
940 Y=FNY(O)-S1/(K5+O)
```

```
950 Ø2=Ø-Z/Y
960 IF Ø2<0 THEN 1010
970 Ø=Ø2
980 NEXT V
990 P=1.1
1000 GØ TØ 5360
1010 FØR V=1 TØ 10
1020 Ø=Ø/(1+Z/Ø/Y)
1030 S1=SO/(1+Ø/K5)
1040 S2=SO/(1+K5/Ø)
1050 GØSUB 5700
1052 IF P9=1 THEN 5410
1055 IF P9=2 THEN 815
1060 Y=FNY(Ø)-S1/(K5+Ø)
1070 NEXT V
1080 P=1.2
1090 GØ TØ 5360
1300 REM,CASO4 PPT ØNLY
1310 M=MO
1320 Ø1=Ø
1330 PO=2
1340 FØR V=1 TØ 10
1350 GØSUB 1550  ! TØ CALCULATE C,S2 AND S1
1360 GØSUB 5700
1362 IF P9=1 THEN 5410
1365 IF P9=2 THEN 815
1370 Y=FNY(Ø)+FNX(Ø)
1380 Ø2=Ø-Z/Y
1390 IF Ø2<0 THEN 1440
1400 Ø=Ø2
1410 NEXT V
1420 P=2.1
1430 GØ TØ 5360
1440 FØR V=1 TØ 10
1450 Ø=Ø/(1+Z/Ø/Y)
1460 GØSUB 1550
1470 GØSUB 5700
1472 IF P9=1 THEN 5410
1475 IF P9=2 THEN 815
1480 Y=FNY(Ø)+FNX(Ø)
1490 NEXT V
1500 P=2.2
1510 GØ TØ 5360
1550 REM ,SUBRØUTINE FØR C,S2 AND S1, WHEN CASO4 PPT
1555 C1=SQR((SO-CO)↑2+4*K6*(1+K5/Ø))
1560 IF SO>CO THEN 1575
1565 C=(CO-SO+C1)/2
1570 GØ TØ 1580
1575 C=2*K6*(1+K5/Ø)/(SO-CO+C1)
1580 S2=K6/C
1585 S1=S2*K5/Ø
```

```
1590 RETURN
1700 IF S0*K4/O/O>K6*(1+K5/O) THEN 2200
1800 REM ,CA(OH)2 PPT ONLY
1810 M=M0
1820 O1=O
1830 P0=3
1840 FOR V=1 TO 10
1850 C=K4/O/O
1860 S1=S0/(1+O/K5)
1870 S2=S0/(1+K5/O)
1880 GOSUB 5700
1882 IF P9=1 THEN 5410
1885 IF P9=2 THEN 815
1890 Y=FNY(O)-S1/(K5+O)-4*C/O
1900 O2=O-Z/Y
1910 IF O2<0 THEN 1960
1920 O=O2
1930 NEXT V
1940 P=3.1
1950 GO TO 5360
1960 FOR V=1 TO 10
1970 O=O/(1+Z/O/Y)
1980 C=K4/O/O
1990 S1=S0/(1+O/K5)
2000 S2=S0/(1+K5/O)
2010 GOSUB 5700
2012 IF P9=1 THEN 5410
2015 IF P9=2 THEN 815
2020 Y=FNY(O)-S1/(K5+O)-4*C/O
2030 NEXT V
2040 P=3.2
2050 GO TO 5360
2200 GOSUB 1550
2210 IF C<K4/O/O THEN 1300
2220 REM ,CASO4 + CA(OH)2 PPT
2230 M=M0
2240 O1=O
2250 P0=4
2260 FOR V=1 TO 10
2270 C=K4/O/O
2280 S2=K6/C
2290 S1=S2*K5/O
2300 GOSUB 5700
2302 IF P9=1 THEN 5410
2305 IF P9=2 THEN 815
2310 Y=FNY(O)-S1/O-4*(S2+C)/O
2320 O2=O-Z/Y
2330 IF O2<0 THEN 2380
2340 O=O2
2350 NEXT V
2360 P=4.1
```

```
2370 GØ TØ 5360
2380 FØR V=1 TØ 10
2390 Ø=Ø/(1+Z/Ø/Y)
2400 C=K4/Ø/Ø
2410 S2=K6/C
2420 S1=S2*K5/Ø
2430 GØSUB 5700
2432 IF P9=1 THEN 5410
2435 IF P9=2 THEN 815
2440 Y=FNY(Ø)-S1/Ø-4*(S2+C)/Ø
2450 NEXT V
2460 P=4.2
2470 GØ TØ 5360
2600 IF CO*Ø*Ø>K4 THEN 3400
2610 IF CO*SO>K6*(1+K5/Ø) THEN 3000
2620 REM ,MG(OH)2 PPT ØNLY
2630 C=CO
2640 Ø1=Ø
2650 PO=5
2660 FØR V=1 TØ 10
2670 M=K3/Ø/Ø
2680 S1=SO/(1+Ø/K5)
2690 S2=SO/(1+K5/Ø)
2700 GØSUB 5700
2702 IF P9=1 THEN 5410
2705 IF P9=2 THEN 815
2710 Y=FNY(Ø)-S1/(K5+Ø)-4*M/Ø
2720 Ø2=Ø-Z/Y
2730 IF Ø2<0 THEN 2780
2740 Ø=Ø2
2750 NEXT V
2760 P=5.1
2770 GØ TØ 5360
2780 FØR V=1 TØ 10
2790 Ø=Ø/(1+Z/Ø/Y)
2800 M=K3/Ø/Ø
2810 S1=SO/(1+Ø/K5)
2820 S2=SO/(1+K5/Ø)
2830 GØSUB 5700
2832 IF P9=1 THEN 5410
2835 IF P9=2 THEN 815
2840 Y=FNY(Ø)-S1/(K5+Ø)-4*M/Ø
2850 NEXT V
2860 P=5.2
2870 GØ TØ 5360
3000 REM ,CASO4 + MG(OH)2  PPT
3010 Ø1=Ø
3020 PO=6
3030 FØR V=1 TØ 10
3040 M=K3/Ø/Ø
3050 GØSUB 1550
```

```
3060 GOSUB 5700
3062 IF P9=1 THEN 5410
3065 IF P9=2 THEN 815
3070 Y=FNY(O)+FNX(O)-4*M/O
3080 O2=O-Z/Y
3090 IF O2<0 THEN 3140
3100 O=O2
3110 NEXT V
3120 P=6.1
3130 GO TO 5360
3140 FOR V=1 TO 10
3150 O=O/(1+Z/O/Y)
3160 M=K3/O/O
3170 GOSUB 1550
3180 GOSUB 5700
3182 IF P9=1 THEN 5410
3185 IF P9=2 THEN 815
3190 Y=FNY(O)+FNX(O)-4*M/O
3200 NEXT V
3210 P=6.2
3220 GO TO 5360
3400 IF S0*K4/O/O>K6*(1+K5/O) THEN 3800
3410 REM ,MG(0H)2 +CA(0H)2 PPT
3420 O1=O
3430 P0=7
3440 FOR V=1 TO 10
3450 M=K3/O/O
3460 C=K4/O/O
3470 S1=S0/(1+O/K5)
3480 S2=S0/(1+K5/O)
3490 GOSUB 5700
3492 IF P9=1 THEN 5410
3495 IF P9=2 THEN 815
3500 Y=FNY(O)-S1/(K5+O)-4*(M+C)/O
3510 O2=O-Z/Y
3520 IF O2<0 THEN 3570
3530 O=O2
3540 NEXT V
3550 P=7.1
3560 GO TO 5360
3570 FOR V=1 TO 10
3580 O=O/(1+Z/O/Y)
3590 M=K3/O/O
3600 C=K4/O/O
3610 S1=S0/(1+O/K5)
3620 S2=S0/(1+K5/O)
3630 GOSUB 5700
3632 IF P9=1 THEN 5410
3634 IF P9=2 THEN 815
3640 Y=FNY(O)-S1/(K5+O)-4*(M+C)/O
3650 NEXT V
```

```
3660 P=7.2
3670 GO TO 5360
3800 GOSUB 1550
3810 IF C<K4/O/O THEN 3000
3820 REM ,CASO4 +CA(OH)2 + MG(OH)2 PPT
3830 O1=O
3840 PO=8
3850 FOR V=1 TO 10
3860 M=K3/O/O
3870 C=K4/O/O
3880 S2=K6/C
3890 S1=S2*K5/O
3900 GOSUB 5700
3902 IF P9=1 THEN 5410
3905 IF P9=2 THEN 815
3910 Y=FNY(O)-S1/O-4*(S2+C+M)/O
3920 O2=O-Z/Y
3930 IF O2<0 THEN 3980
3940 O=O2
3950 NEXT V
3960 P=8.1
3970 GO TO 5360
3980 FOR V=1 TO 10
3990 O=O/(1+Z/O/Y)
4000 M=K3/O/O
4010 C=K4/O/O
4020 S2=K6/C
4030 S1=S2*K5/O
4040 GOSUB 5700
4042 IF P9=1 THEN 5410
4045 IF P9=2 THEN 815
4050 Y=FNY(O)-S1/O-4*(S2+C+M)/O
4060 NEXT V
4070 P=8.2
4080 GO TO 5360
5360 PRINT USING 5370,P
5370 :P=##.###
5380 GO TO 5410
5400 REM
5410 IF O↑2>K1 THEN 5440
5420 E=O
5430 GO TO 5450
5440 E=K1/O
5450 T2=T1
5460 PRINT USING 1,T2,K1/O,O,C,M,S2,S1,Z/E
5470 P1=-LGT(K1/O)!PH
5480 PUT 1:T2,B,B1,H,H1,L,R,P1
5490 REM GO TO NEXT C.F.
5500 REM
5510 NEXT T3
5520 OPEN 2,'FILE9',INPUT
```

```
5530 PRINT
5540 PRINT USING 140
5550 ON EOF 2 GO TO 8000
5560 GET 2:T2,B,B1,H,H1,L,R,P1
5570 PRINT USING 3,T2,B,B1,H,H1,L,R,P1
5580 GO TO 5560
5700 REM, CALCULATE  Z  AND TEST ACCURACY
5702 I1=I
5705 P9=0
5963 L=N+B1+K1/O+2*(M+C)
5965 R=L1+S1+O+H1+2*S2
5970 Z=L-R
5980 IF ABS(Z)>E9 THEN 6060
5985 I=FNI(O)
5987 IF ABS(I-I1)>I*E8 THEN 6010
5990 IF ABS(O-O1)<O*E8 THEN 6052
6010 GOSUB 510
6015 GOSUB 750
6020 U=U+1
6030 IF U<101 THEN 6056
6040 P=P0+0.4
6050 GO TO 5360
6052 P9=1
6054 GO TO 6060
6056 P9=2
6060 RETURN
8000 END
```

ISOLATED CAVITY MODEL

```
1 :#.###-#.#!!!!-#.##!!!!-#.###!!!!-#.###!!!!-#.###!!!!-#.###!!!!-#.!!!!

3 :#.###-#.#!!!!-#.##!!!!-#.###!!!!-#.###!!!!-#.###!!!!-#.###!!!!-##.###

5 E8=0.0023
10 E9=1.E-11
15 DEF FNI(O)=2*(C+M+S2)+(N+L1+S1+K1/O+O+H1+B1)/2
52 DEF FNX(O)=S1*(S1/(C+S1+S2)-1)/O
54 DEF FNY(O)=(-1-K1/O/O)
130 :LGCF  [H]      [OH]       [CA]       [MG]       [SO4]      [HSO4]     Z/E

140 :LGCF [AMINE]T [AMINE]+  [CO2]T     [HCO3]     [CATIONS] [ANIONS]    PH

150 :################### WITH ###################
160 T=273+280
170 D7=800
180 OPEN 1,'FILE9',OUTPUT
190 OPEN 5,'FILES',OUTPUT
200 Q1=10↑(-151.713/T-111.491-.03685*T+44.077*LGT(T))
210 Q4=10↑(-25.7085+12.9722*LGT(T)-530.49/T-.032331*T)
220 Q3=Q4*10↑(-5.6)
230 Q5=10↑(91.471-33.0024*LGT(T)-3520.3/T)
240 Q6=10↑(-133.207+53.5472*LGT(T)+3569.6/T-.0529025*T)
250 Q7=10↑(-2382.2/T+8.153-.02194*T)
260 REM READ K AMINE,VAP/LIQ RATIO,CONC.,NAME
270 DATA 6.7608E-7,3.7,1.45E-5
280 READ Q2 ,D2,BO
290 A$='AMMONIA'
300 REM READ NA,CL,MG,CA,S4,HCO3
310 DATA 2.08E-7,4.98E-8,2.27E-7,5.32E-7,1.72E-7,1.31E-6,1.47E-5
320 READ N9,LO,M9,C9,S9,HO
330 B$='ALKALINE FRESH'
340 PUT 5:B$,A$
350 REM INITIALIZING
360 TO=1
370 NO=N9*TO
380 L1=LO*TO
390 MO=M9*TO
400 CO=C9*TO
405 SO=S9*TO
406 N=NO
410 M=MO
420 C=CO
430 S1=SO
440 O=SQR(Q1)
450 PRINT USING 150,B$,A$
460 PRINT
470 PRINT USING 130
480 I=FNI(O)
490 GOSUB 510
500 GO TO 600
```

```
510 REM TØ REDEFINE K'S
520 K1=Q1*10↑(5.36*SQR(I)/(1+SQR(I))-(.6356-.001078*T)*I)
530 K2=Q2*10↑(2.396*SQR(I)/(1+1.5*SQR(I)))
540 K4=Q4*10↑(7.722*SQR(I)/(1+2.16*SQR(I))-.16*I+.0125*I↑2)
550 K3=K4*10↑(-5.6)
560 K5=K1/(Q5*10↑(4.792*SQR(I)/(1+1.76*SQR(I))))
570 K6=Q6*10↑(9.584*SQR(I)/(1+1.51*SQR(I)))
580 K7=K1/Q7
590 RETURN
600 FØR T3=1 TØ 4
601 V4=10↑(T3-4)
602 V5=9*V4
603 IF T3<4 THEN 605
604 V5=4*V4
605 FØR T4=V4 TØ V5 STEP V4
606 T5=T0
607 T0=10↑T4
610 REM SØLUTIØN CØNTENTS PER KG.
620 N=N9*T0
630 L1=L0*T0
640 M0=M9*T0
650 C0=C9*T0
660 S0=S9*T0
700 U=1
720 GØSUB 510
730 GØSUB 750
740 GØ TØ 815
750 F2=Ø/(K2+Ø)
760 F7=K7/(K7+Ø)
770 B=B0*(T5/T0)↑(F2*D2-1)
780 H=H0*(T5/T0)↑(F7*D7-1)
790 B1=(1-F2)*B
800 H1=(1-F7)*H
810 RETURN
815 REM
820 IF M0*Ø*Ø>K3 THEN 2600
830 IF C0*Ø*Ø>K4 THEN 1700
840 IF C0*S0>K6*(1+K5/Ø) THEN 1300
850 REM NØ PPT
860 M=M0
870 C=C0
880 Ø1=Ø
890 P0=1
900 FØR V=1 TØ 20
910 S1=S0/(1+Ø/K5)
920 S2=S0/(1+K5/Ø)
930 GØSUB 5700    !TØ CALCULATE  Z  AND TØ TEST ACCURACY
932 IF P9=1 THEN 5410
935 IF P9=2 THEN 815
940 Y=FNY(Ø)-S1/(K5+Ø)
950 Ø2=Ø-Z/Y
```

```
960 IF 02<0 THEN 1010
970 0=02
980 NEXT V
990 P=1.1
1000 GO TO 5360
1010 FOR V=1 TO 10
1020 0=0/(1+Z/0/Y)
1030 S1=SO/(1+0/K5)
1040 S2=SO/(1+K5/0)
1050 GOSUB 5700
1052 IF P9=1 THEN 5410
1055 IF P9=2 THEN 815
1060 Y=FNY(0)-S1/(K5+0)
1070 NEXT V
1080 P=1.2
1090 GO TO 5360
1300 REM,CASO4 PPT ONLY
1310 M=MO
1320 01=0
1330 PO=2
1340 FOR V=1 TO 10
1350 GOSUB 1550  ! TO CALCULATE C,S2 AND S1
1360 GOSUB 5700
1362 IF P9=1 THEN 5410
1365 IF P9=2 THEN 815
1370 Y=FNY(0)+FNX(0)
1380 02=0-Z/Y
1390 IF 02<0 THEN 1440
1400 0=02
1410 NEXT V
1420 P=2.1
1430 GO TO 5360
1440 FOR V=1 TO 10
1450 0=0/(1+Z/0/Y)
1460 GOSUB 1550
1470 GOSUB 5700
1472 IF P9=1 THEN 5410
1475 IF P9=2 THEN 815
1480 Y=FNY(0)+FNX(0)
1490 NEXT V
1500 P=2.2
1510 GO TO 5360
1550 REM ,SUBROUTINE FOR C,S2 AND S1, WHEN CASO4 PPT
1555 C1=SQR((SO-CO)↑2+4*K6*(1+K5/0))
1560 IF SO>CO THEN 1575
1565 C=(CO-SO+C1)/2
1570 GO TO 1580
1575 C=2*K6*(1+K5/0)/(SO-CO+C1)
1580 S2=K6/C
1585 S1=S2*K5/0
1590 RETURN
```

```
1700 IF SO*K4/Ø/Ø>K6*(1+K5/Ø) THEN 2200
1800 REM ,CA(OH)2 PPT ØNLY
1810 M=MO
1820 Ø1=Ø
1830 PO=3
1840 FØR V=1 TØ 10
1850 C=K4/Ø/Ø
1860 S1=SO/(1+Ø/K5)
1870 S2=SO/(1+K5/Ø)
1880 GØSUB 5700
1882 IF P9=1 THEN 5410
1885 IF P9=2 THEN 815
1890 Y=FNY(Ø)-S1/(K5+Ø)-4*C/Ø
1900 Ø2=Ø-Z/Y
1910 IF Ø2<0 THEN 1960
1920 Ø=Ø2
1930 NEXT V
1940 P=3.1
1950 GØ TØ 5360
1960 FØR V=1 TØ 10
1970 Ø=Ø/(1+Z/Ø/Y)
1980 C=K4/Ø/Ø
1990 S1=SO/(1+Ø/K5)
2000 S2=SO/(1+K5/Ø)
2010 GØSUB 5700
2012 IF P9=1 THEN 5410
2015 IF P9=2 THEN 815
2020 Y=FNY(Ø)-S1/(K5+Ø)-4*C/Ø
2030 NEXT V
2040 P=3.2
2050 GØ TØ 5360
2200 GØSUB 1550
2210 IF C<K4/Ø/Ø THEN 1300
2220 REM ,CASO4 + CA(OH)2 PPT
2230 M=MO
2240 Ø1=Ø
2250 PO=4
2260 FØR V=1 TØ 10
2270 C=K4/Ø/Ø
2280 S2=K6/C
2290 S1=S2*K5/Ø
2300 GØSUB 5700
2302 IF P9=1 THEN 5410
2305 IF P9=2 THEN 815
2310 Y=FNY(Ø)-S1/Ø-4*(S2+C)/Ø
2320 Ø2=Ø-Z/Y
2330 IF Ø2<0 THEN 2380
2340 Ø=Ø2
2350 NEXT V
2360 P=4.1
2370 GØ TØ 5360
```

```
2380 FØR V=1 TØ 10
2390 Ø=Ø/(1+Z/Ø/Y)
2400 C=K4/Ø/Ø
2410 S2=K6/C
2420 S1=S2*K5/Ø
2430 GØSUB 5700
2432 IF P9=1 THEN 5410
2435 IF P9=2 THEN 815
2440 Y=FNY(Ø)-S1/Ø-4*(S2+C)/Ø
2450 NEXT V
2460 P=4.2
2470 GØ TØ 5360
2600 IF CO*Ø*Ø>K4 THEN 3400
2610 IF CO*SO>K6*(1+K5/Ø) THEN 3000
2620 REM ,MG(OH)2 PPT ØNLY
2630 C=CO
2640 Ø1=Ø
2650 PO=5
2660 FØR V=1 TØ 10
2670 M=K3/Ø/Ø
2680 S1=SO/(1+Ø/K5)
2690 S2=SO/(1+K5/Ø)
2700 GØSUB 5700
2702 IF P9=1 THEN 5410
2705 IF P9=2 THEN 815
2710 Y=FNY(Ø)-S1/(K5+Ø)-4*M/Ø
2720 Ø2=Ø-Z/Y
2730 IF Ø2<0 THEN 2780
2740 Ø=Ø2
2750 NEXT V
2760 P=5.1
2770 GØ TØ 5360
2780 FØR V=1 TØ 10
2790 Ø=Ø/(1+Z/Ø/Y)
2800 M=K3/Ø/Ø
2810 S1=SO/(1+Ø/K5)
2820 S2=SO/(1+K5/Ø)
2830 GØSUB 5700
2832 IF P9=1 THEN 5410
2835 IF P9=2 THEN 815
2840 Y=FNY(Ø)-S1/(K5+Ø)-4*M/Ø
2850 NEXT V
2860 P=5.2
2870 GØ TØ 5360
3000 REM ,CASO4 + MG(OH)2  PPT
3010 Ø1=Ø
3020 PO=6
3030 FØR V=1 TØ 10
3040 M=K3/Ø/Ø
3050 GØSUB 1550
3060 GØSUB 5700
```

```
3062 IF P9=1 THEN 5410
3065 IF P9=2 THEN 815
3070 Y=FNY(O)+FNX(O)-4*M/O
3080 O2=O-Z/Y
3090 IF O2<0 THEN 3140
3100 O=O2
3110 NEXT V
3120 P=6.1
3130 GO TO 5360
3140 FOR V=1 TO 10
3150 O=O/(1+Z/O/Y)
3160 M=K3/O/O
3170 GOSUB 1550
3180 GOSUB 5700
3182 IF P9=1 THEN 5410
3185 IF P9=2 THEN 815
3190 Y=FNY(O)+FNX(O)-4*M/O
3200 NEXT V
3210 P=6.2
3220 GO TO 5360
3400 IF SO*K4/O/O>K6*(1+K5/O) THEN 3800
3410 REM ,MG(OH)2 +CA(OH)2 PPT
3420 O1=O
3430 PO=7
3440 FOR V=1 TO 10
3450 M=K3/O/O
3460 C=K4/O/O
3470 S1=SO/(1+O/K5)
3480 S2=SO/(1+K5/O)
3490 GOSUB 5700
3492 IF P9=1 THEN 5410
3495 IF P9=2 THEN 815
3500 Y=FNY(O)-S1/(K5+O)-4*(M+C)/O
3510 O2=O-Z/Y
3520 IF O2<0 THEN 3570
3530 O=O2
3540 NEXT V
3550 P=7.1
3560 GO TO 5360
3570 FOR V=1 TO 10
3580 O=O/(1+Z/O/Y)
3590 M=K3/O/O
3600 C=K4/O/O
3610 S1=SO/(1+O/K5)
3620 S2=SO/(1+K5/O)
3630 GOSUB 5700
3632 IF P9=1 THEN 5410
3634 IF P9=2 THEN 815
3640 Y=FNY(O)-S1/(K5+O)-4*(M+C)/O
3650 NEXT V
3660 P=7.2
```

```
3670 GO TO 5360
3800 GOSUB 1550
3810 IF C<K4/O/O THEN 3000
3820 REM ,CASO4 +CA(OH)2 + MG(OH)2 PPT
3830 O1=0
3840 PO=8
3850 FOR V=1 TO 10
3860 M=K3/O/O
3870 C=K4/O/O
3880 S2=K6/C
3890 S1=S2*K5/O
3900 GOSUB 5700
3902 IF P9=1 THEN 5410
3905 IF P9=2 THEN 815
3910 Y=FNY(O)-S1/O-4*(S2+C+M)/O
3920 O2=O-Z/Y
3930 IF O2<0 THEN 3980
3940 O=O2
3950 NEXT V
3960 P=8.1
3970 GO TO 5360
3980 FOR V=1 TO 10
3990 O=O/(1+Z/O/Y)
4000 M=K3/O/O
4010 C=K4/O/O
4020 S2=K6/C
4030 S1=S2*K5/O
4040 GOSUB 5700
4042 IF P9=1 THEN 5410
4045 IF P9=2 THEN 815
4050 Y=FNY(O)-S1/O-4*(S2+C+M)/O
4060 NEXT V
4070 P=8.2
4080 GO TO 5360
5360 PRINT USING 5370,P
5370 :P=##.###
5380 GO TO 5410
5400 REM
5410 IF O↑2>K1 THEN 5440
5420 E=O
5430 GO TO 5450
5440 E=K1/O
5450 T2=LGT(TO)
5460 PRINT USING 1,T2,K1/O,O,C,M,S2,S1,Z/E
5470 P1=-LGT(K1/O)!PH
5480 PUT 1:T2,B,B1,H,H1,L,R,P1
5490 REM GO TO NEXT C.F.
5492 HO=H
5493 BO=B
5498 NEXT T4
5500 REM
```

```
5510 NEXT T3
5520 OPEN 2,'FILE9',INPUT
5530 PRINT
5540 PRINT USING 140
5550 ON EOF 2 GO TO 8000
5560 GET 2:T2,B,B1,H,H1,L,R,P1
5570 PRINT USING 3,T2,B,B1,H,H1,L,R,P1
5580 GO TO 5560
5700 REM, CALCULATE  Z  AND TEST ACCURACY
5702 I1=I
5705 P9=0
5963 L=N+B1+K1/O+2*(M+C)
5965 R=L1+S1+O+H1+2*S2
5970 Z=L-R
5980 IF ABS(Z)>E9 THEN 6060
5985 I=FNI(O)
5987 IF ABS(I-I1)>I*E8 THEN 6010
5990 IF ABS(O-O1)<O*E8 THEN 6052
6010 GOSUB 510
6015 GOSUB 750
6020 U=U+1
6030 IF U<101 THEN 6056
6040 P=P0+0.4
6050 GO TO 5360
6052 P9=1
6054 GO TO 6060
6056 P9=2
6060 RETURN
8000 END
```