

NWT 160
June 1980

NORTH ANNA OPERATIONAL
BACKGROUND CHEMISTRY REVIEW

S. G. Sawochka
W. L. Pearl

Prepared for Virginia Electric & Power Company
Purchase Order No. 21139



Corporation

7015 REALM DRIVE, SAN JOSE, CALIFORNIA 95119

8006259 143

This document was prepared for Virginia
Electric & Power Company. Neither NWT
Corporation nor any person acting on
its behalf assumes any responsibility
for liability or damage which may result
from the use of any information disclosed
in this document.



NORTH ANNA OPERATIONAL BACKGROUND CHEMISTRY REVIEW

BACKGROUND

The North Anna Nuclear Generating Station of Virginia Electric & Power Company (Vepco) is located on the southern shore of Lake Anna in Louisa County, Virginia. The plant has been operational since April 1978. The first scheduled refueling outage began on September 25, 1979. During that outage, a routine steam generator inspection was planned. However, extensive support plate corrosion consistent with the early stages of denting, was detected dictating a more extensive inspection (Table 1). Inspection results were as follows¹:

Steam Generator A: "No indications of tube defects were observed with the 400 kHz and 100 kHz EC probes. Approximately 36 percent of the tubes inspected with the 7.5 kHz probe exhibited signs of tube/support plate intersection corrosion and/or possible ligament cracking."

Steam Generator B: "No indications of tube defects were observed with the 400 kHz and 100 kHz EC probes. Almost 16 percent of the tubes inspected with the 7.5 kHz probe exhibited support plate corrosion or possible ligament cracking."

Steam Generator C: "Two leakers were detected in row 1, columns 50 and 61 in SG 'C'. One restricted tube was detected in row 46, column 41. Approximately 37 percent of the tubes inspected with the 7.5 kHz probe showed indications of support plate corrosion or possible ligament cracking."

Summary: "Of the approximately 1070 tubes inspected in three SG's with the 400 kHz probe, 2 tubes were identified as leakers."

"Approximately 34 percent of the 910 tubes inspected with the 7.5 kHz probe in three SG's indicated support plate/tube intersection corrosion and/or possible ligament cracking. Most of the tubes inspected with the 7.5 kHz probe showed some indication of minor support plate/tube intersection corrosion."

"One tube in SG 'C' was found to be slightly restricted in Row 46, column 41. It would pass a 650 mil probe, but not a 700 mil probe. Tube nominal ID is 775 mils."

"The extensive inspections performed with the 7.5 kHz EC probe indicated minor corrosion in the tube to support plate annuli. The corrosion observed appears to be the very early stages of the denting phenomenon affecting some other plants, especially those with salt water cooling."



TABLE 1
NORTH ANNA UNIT 1
EXPANDED STEAM GENERATOR INSPECTION PROGRAM

<u>Steam Generator</u>	<u>EC Probe</u>	<u>Tubes Inspected</u>	<u>Indications</u>
A	400 kHz*	440	None
	100 kHz (diff)	181 (rows 1 & 2)	None
	7.5 kHz	370	132
B	400 kHz	133	None
	100 kHz (diff)	88 (row 1)	None
	100 kHz (abs)	89 (row 1)	None
	7.5 kHz	119	19
C	400 kHz*	480	2 (leakers)
	400 kHz	163 (cold leg)	None
	100 kHz (diff)	178 (rows 1 & 2)	2 (same leakers)
	100 kHz (abs)	117 (vicinity of leakers)***	2 (same leakers)
	7.5 kHz**	421	155

*Initial Regulatory Guide Inspection

**Additional Initial Inspection

***117 Tubes Including Leakers

Numbers are approximate and data are still being reviewed. A final report will be issued for retention in station records.



In light of the eddy current observations, several reviews of secondary chemistry at North Anna were performed, and recommendations solicited from Westinghouse relative to a future course of action. A major conclusion of the reviews was that the corrosion attack probably was related to an ingress of powdered resin into the steam generators from the condensate filters. This incident is described in Appendix A.¹ Chemistry effects of the resin intrusion and the major findings of a Westinghouse data review subsequently were addressed by the Vepco staff and are summarized in Appendix B.¹

To further evaluate possible effects of the resin intrusion incident(s) on the North Anna steam generator corrosion, NWT was retained to perform an independent review of secondary system chemistry control at North Anna. Results of this review are presented herein.



SYSTEM DESIGN AND DESCRIPTION

North Anna Unit 1 is a 907 MWe Westinghouse PWR with 3 U-tubed steam generators. Tubes are Alloy 600, and support plates are drilled carbon steel. The plant was engineered and constructed by Stone & Webster. Condenser cooling water is taken from Lake Anna. The water is of high quality (Table 2), but it is relatively rich in sulfate.

A schematic of the secondary system is shown in Figure 1. The condenser is tubed with stainless steel. Heater tubing materials are as follows:

1st point	80/20 CuNi
2nd point	90/10 CuNi
3rd point	Arsenical Admiralty
4th point	Arsenical Admiralty
5th point	Arsenical Admiralty
6th point	Arsenical Admiralty
Air Ejector	304 Stainless (316 stainless nozzles)
Condenser	304 Stainless
Gland Steam	90/10 CuNi

Three half capacity condensate pumps draw from two hotwells. Until the 1980 startup, the condensate was processed through Graver powdered resin filters. Because of the possibility that resin leakage was associated with the steam generator corrosion detected in 1979, the filters currently are bypassed. Each filter vessel has 420 non-segmented polypropylene septums. Specific flowrate is approximately 3 gpm/ft². Typically, filters are precoated with 6 bags of hydrogen form cation resin, 5 bags of ammonium form cation resin and 6 bags of hydroxide form anion resin (cation to anion dry weight ratio of 3:1 and total dry precoat weight of 296 lbs).

A precoat (V/V)₅ of 50% ±5% is sought during normal operation. Tighter precoats are employed during startups or transients (increased "Solution A"). Ecodex, a fiber-resin mixture, also has been employed during startups. This gives improved suspended solids removal but higher differential pressure drops.

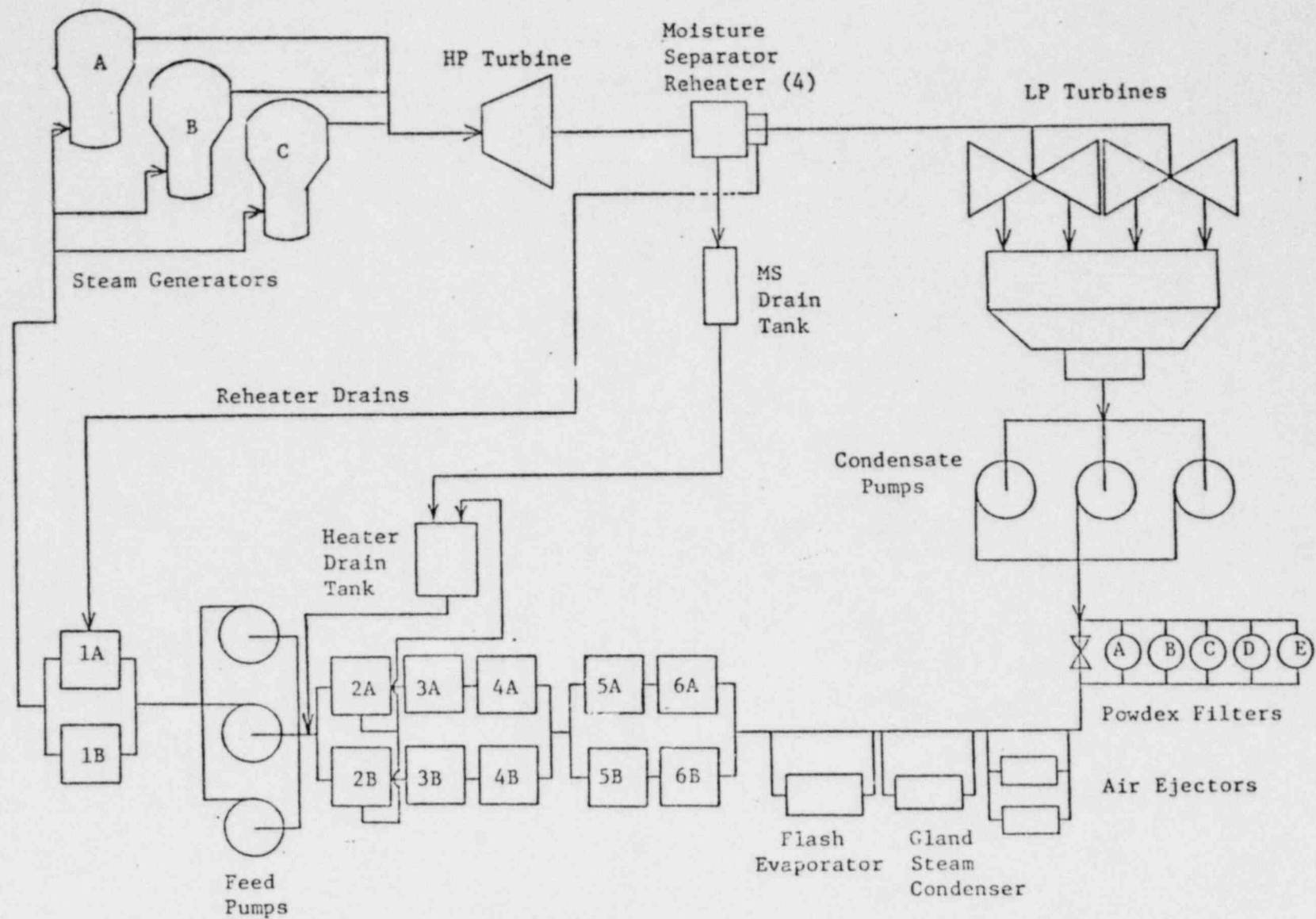


Figure 1. North Anna Secondary System Schematic

TABLE 1
NORTH ANNA WATER CHEMISTRY

Date	Calcium ppm	Magnesium ppm	Hardness, ppm as CaCO ₃	Bicarbonate ppm	Chloride ppm	Sulfate ppm	Silica ppm	Suspended Solids ppm	Copper ppm	Iron ppm	Phosphate ppm	Nitrate ppm	Conductivity µmhos/cm	pH
9/28/78	5	2	20	20			3.7	5		0.15	<0.05			7.2
11/1	5	2	20		3	10	4.4	5	<0.05	0.25	<0.05			7.1
11/1	5.12	2.05			3.5		5.35		0.01	0.37				
12/4	5	2	22	18	3.0	10	5.0	<5	<0.05	0.30	<0.05		71	6.8
12/4	5.12	2.04			2.5		5.88		0.01	0.26				
1/2/79	5	3	26	20	3.4	10	4.1	15	<0.05	0.30	<0.05		70	7.1
1/2	5.25	2.08			3.5	12.5	4.28		0.01	0.24	0.181			7.1
2/6	4	2	18	14	3.3	10	4.8	<5	<0.05	0.15	0.05		60	7.2
2/6	4.88	1.96			2.75	9.5	0.75		0.01	0.14	0.028		67	7.26
3/1	6.88	1.80			3.13	7.3	0.22		0.02	0.76	0.174		65	6.22
3/15	2	4	20	14	3.2	10	6.2	10	<0.05	0.20	0.05	1.7	56	6.7
4/2	2.4	1.92			3.0	14	3.75		0.01	0.21	2.30			7.1
5/3	4.12	1.71			2.25	8.3	0.25		0.01	0.34			55	6.92
6/1	4.51				3.25	7.5	0.30		0.01	0.26	0.292		55.5	7.57
7/3	5	4	28	22	3.5	10	3.7	<5	<0.05	0.25	<0.05	0.9	59	7.1
7/5	4.52				2.99	7.5	3.02		0.004	0.43	0.307		58	7.61



CHEMISTRY MONITORING

A. Continuous Monitoring Instrumentation

Secondary cycle in-line chemistry monitors are listed in Table 3. Table 4 lists the instrument manufacturer and range. Cation conductivity is recorded for the steam generator blowdown, condensate, and Powdex system effluent. A recorder is provided with the sodium analyzer on the Powdex system effluent only. Sodium readings from the steam generator blowdown Calgon analyzers are recorded in the daily chemistry logs.

B. Analytical Procedures

Routine analyses for pH, cation conductivity, sodium, chloride, boron, silica, ammonia, hydrazine, oxygen, iron and copper are performed for various locations throughout the secondary side (Table 5). Analytical techniques are shown in Table 6. Blowdown analyses for all species except iron and copper are performed daily. Although a detailed review was not performed of calibration techniques, etc., procedures and analysis frequency appear adequate for monitoring steam generator chemistry.

C. Specifications

Current secondary system operating guidelines for condensate, feedwater and steam generator blowdown are shown in Table 7 for operation with and without boric acid. The only difference between the two guidelines is pH, and of course, boron concentration in the generator.



TABLE 3
IN-LINE CHEMISTRY MEASUREMENTS - SECONDARY CYCLE

<u>Sample</u>	<u>pH</u>	<u>Specific</u>	<u>Cation</u>	<u>Discolved Oxygen</u>	<u>Sodium</u>
S/G Blowdown A, B, and C	X	N	XR	X	X
Condensate	X	XR	XR	X	X
Feedwater	X	XR	N	X	N
Powdex Effluent	X	N	XR	N	XR

X = Analyzer

R = Recorder

N = none

TABLE 4
SECONDARY CYCLE CHEMISTRY INSTRUMENTATION

<u>Variable</u>	<u>Analyzer</u>	<u>Range</u>
Dissolved Oxygen	Hays	0-100 ppb
Specific and Cation Conductivity	Leeds & Northrup*	0-10 μ mhos
Sodium	Calgon 2000	1-100 ppb

*Exception - Secondary Demineralizer

Beckman Solu-meter 0 to 1.0 μ mhos



TABLE 5
STEAM SIDE LABORATORY ANALYSIS

<u>Location</u>	<u>Parameter</u>	<u>Frequency</u>
Steam Generator Blowdown	pH	Daily
	Conductivity	Daily
	Cation Conductivity	Daily
	Sodium	Daily
	Chloride	Daily
	Boron	Daily
	Silica	Daily
	Ammonia	Daily
	Hydrazine	Daily
	Oxygen	Daily
Feedwater	Fe/Cu	Monday
	pH	Daily
	Conductivity	Daily
	Cation Conductivity	Daily
	Ammonia	Daily
	Hydrazine	Daily
	Silica	Daily
	Oxygen	Daily
Condensate	Fe/Cu	Monday
	pH	Daily
	Conductivity	Daily
	Cation Conductivity	Daily
	Sodium	Daily
	Ammonia	Daily
	Hydrazine	Daily
	Silica	Daily
	Chloride	Daily
Main Steam	Fe/Cu	Monday
	pH	Wednesday
	Conductivity	Wednesday
	Ammonia	Wednesday
	Silica	Wednesday
	Sodium	Wednesday



TABLE 5 (cont)

<u>Location</u>	<u>Parameter</u>	<u>Frequency</u>
Powdex Effluent	Sodium	Daily
	Silica	Mon., Wed., Fri.
	Fe and Cu	Monday
Flash Evaporator Dist.	pH	Daily
	Conductivity	Daily
	Chloride/Fluoride	Daily
	Sodium	Daily
	Silica	Daily
Flash Evaporator Demin. Out.	pH	Daily
	Conductivity	Daily
	Silica	Daily
	Sodium	Daily
	Chloride/Fluoride	Daily
Brine	pH	Daily
	Conductivity	Daily
Other Secondary	Bearing Cooling	As required
	Service Water Reservoir	As required
	Air Conditioning, etc.	As required



TABLE 6
NORTH ANNA ANALYTICAL CHEMISTRY PROCEDURES

<u>Species</u>	<u>Technique</u>
Ammonia	Nesslerization
Chloride	Mercuric thiocyanate
Conductivity	Wheatstone Bridge
Fluoride	Specific Ion Electrode
Oxygen	Indigo Carmine or Winkler
pH	Electrode
Suspended Solids	Filtration
Dissolved Solids	Evaporation
Soluble Silica	Ammonium Molybdate



TABLE 7¹

WESTINGHOUSE SECONDARY SYSTEM CHEMISTRY AVT OPERATING GUIDELINES
FOR NORTH ANNA UNIT 1

	<u>Without Boric Acid</u>	<u>With Boric Acid</u>
<u>Condensate</u> ¹		
Oxygen, ppb	<10	<10
<u>Feedwater</u>		
pH, @ 25°C	8.8 - 9.2	>8.0
Conductivity, μmhos	1.8 - 5.0	≤5
Oxygen, ppb	<5	<5
Hydrazine, ppb	[O ₂] + ≥10	[O ₂] + ≥10
Ammonia, ppm	≤0.5	≤0.5

Steam Generator AVT Chemistry Guidelines

<u>Parameter</u>	<u>In the Absence of Locatable Condenser Leakage</u>		<u>In the Presence of Locatable Condenser Leakage</u>	
	<u>Without Boric Acid</u>	<u>With Boric Acid</u>	<u>Without Boric Acid</u> ²	<u>With Boric Acid</u> ³
pH @ 25°C	>8.5	>7.0	>8.5	>7.0
Cation Conductivity μmhos/cm @ 25°C	<2.0	<2.0	2.0	2.0
Boron, ppm	NA	5-10	NA	5-10
Sodium, ppm	<0.04	<0.04	0.1	0.1
Chloride, ppm	<0.05	<0.05	0.15	0.15
Oxygen, ppb	<5	<5	<5	<5
Hydrazine, ppb	[O ₂] + ≥20	[O ₂] + ≥20	[O ₂] + ≥20	[O ₂] + ≥20
Ammonia, ppm	>0.06	>0.06	>0.06	>0.06
Silica, ppm	<0.05	<0.05	0.05	0.05
Blowdown, gpm	Continuous ³	Continuous ³	Continuous ⁴	Continuous ⁴

1. Continuous overboard at air ejector drains.
2. Continued operation with locatable contaminant ingress is not recommended.
3. Operate at the minimum continuous blowdown rate required to maintain continuous monitoring capability, approximately 5 gpm/SG.
4. Blowdown continuously at a rate required to maintain chemistry parameters.



SECONDARY SYSTEM CHEMISTRY

Because of the possible effects of resin intrusion on steam generator corrosion, and the several such incidents reported at North Anna, a brief summary of resin ingress effects on blowdown chemistry is warranted.

Cation resin, which is a sulfonated polystyrene/divinylbenzene copolymer, decomposes to yield sulfuric acid as an end product. Therefore, as a result of cation resin ingress, a depression in steam generator pH will occur concurrent with an increase in cation conductivity reflecting the formation of sulfate ion. During anion resin ingress, tertiary amines, methyl alcohol, and a variety of other organic compounds are formed. These decomposition products generally can be considered volatile, i.e., they are steam distilled from the steam generator. Decomposition of the polystyrene/divinylbenzene matrix also occurs leading to formation of a variety of aliphatic and aromatic organics. These compounds also should volatilize and have a negligible long term impact on steam generator chemistry.

Recent data on resin decomposition at steam generator operating conditions (collected by Combustion Engineering and Battelle Northwest under EPRI contract) are consistent with the above general description of the decomposition process. Based on this description, the expected effect of resin ingress should be a rapid decrease in pH and an increase of cation conductivity. No major change in sodium or chloride level is expected unless significant resin exhaustion to cooling water contaminants has occurred prior to the ingress. Thus, the concurrent variation of blowdown pH, cation conductivity, and sodium level can be used to distinguish probable resin intrusion incidents from those caused by other factors.

Steam generator A blowdown chemistry for 1978, 1979 and 1980 is shown in Figures 2A through 2C, respectively. Similar data for generator B blowdown is shown in Figures 3A through 3C and for generator C in Figures 4A through 4C.

Chemistry during April/May 1978 was not evaluated in detail because of the unstable power pattern; as such, minor resin intrusion incidents could

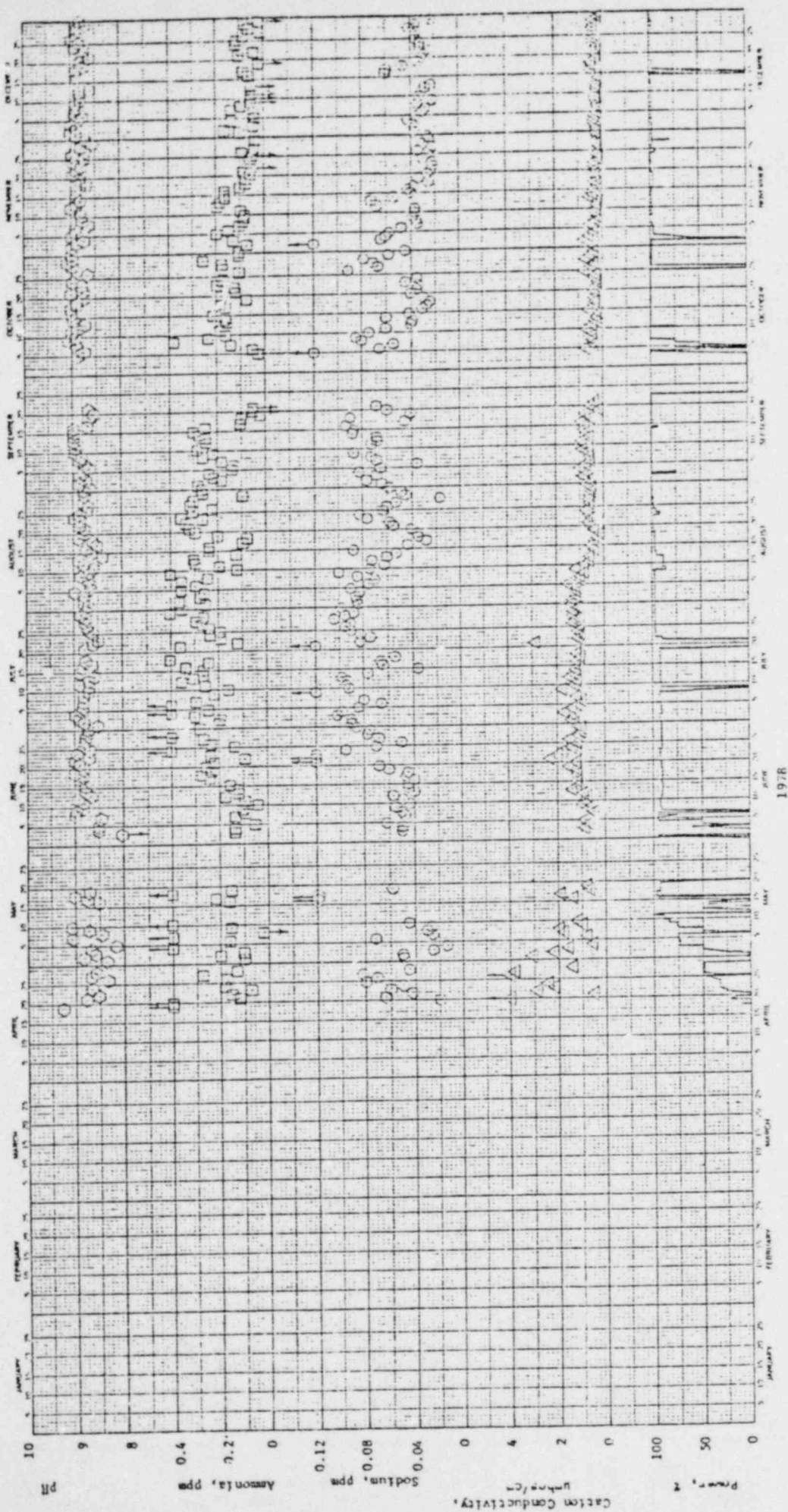


Figure 2A. Steam Generator A Blowdown Chemistry

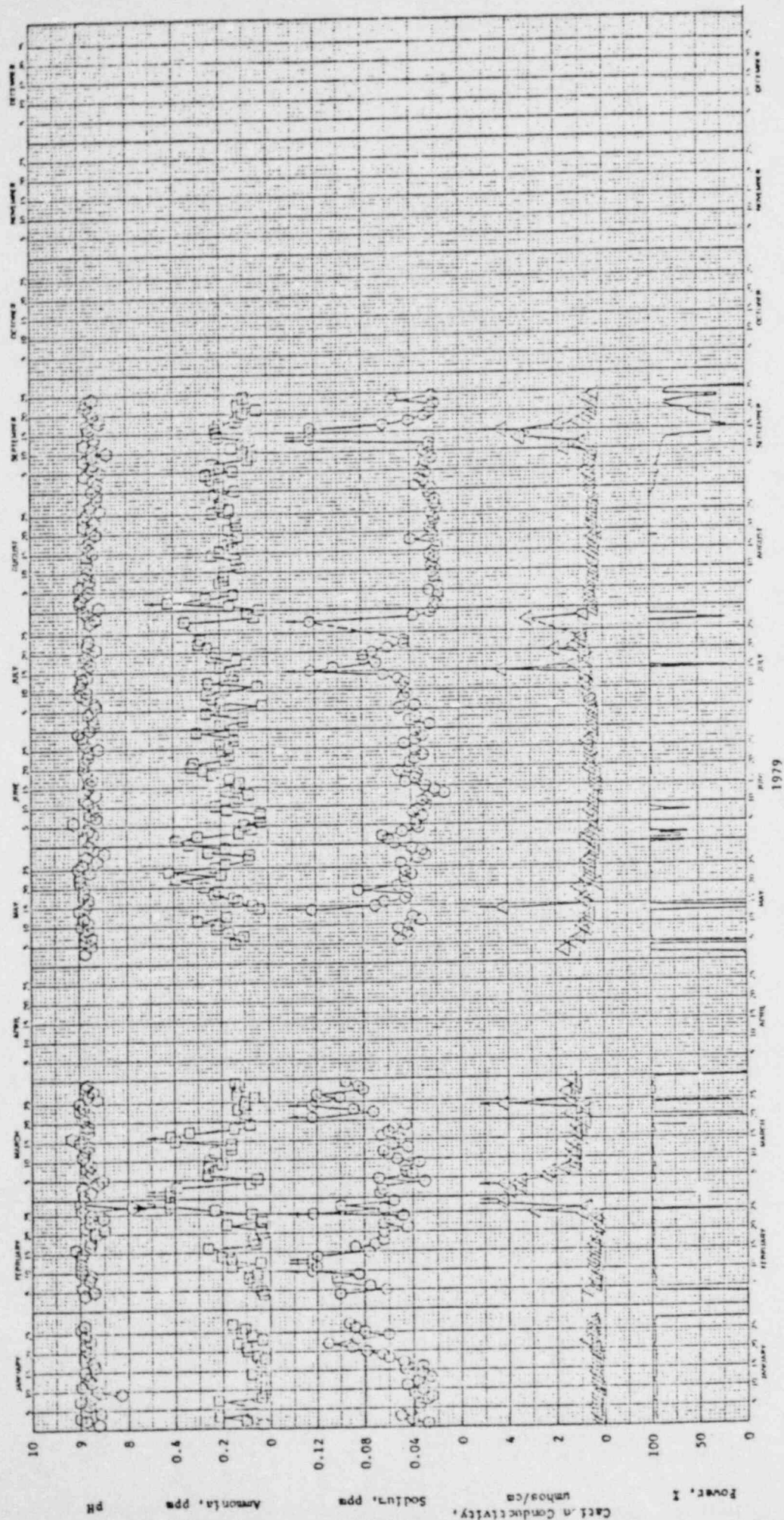


Figure 2B. Steam Generator A Blowdown Chemistry

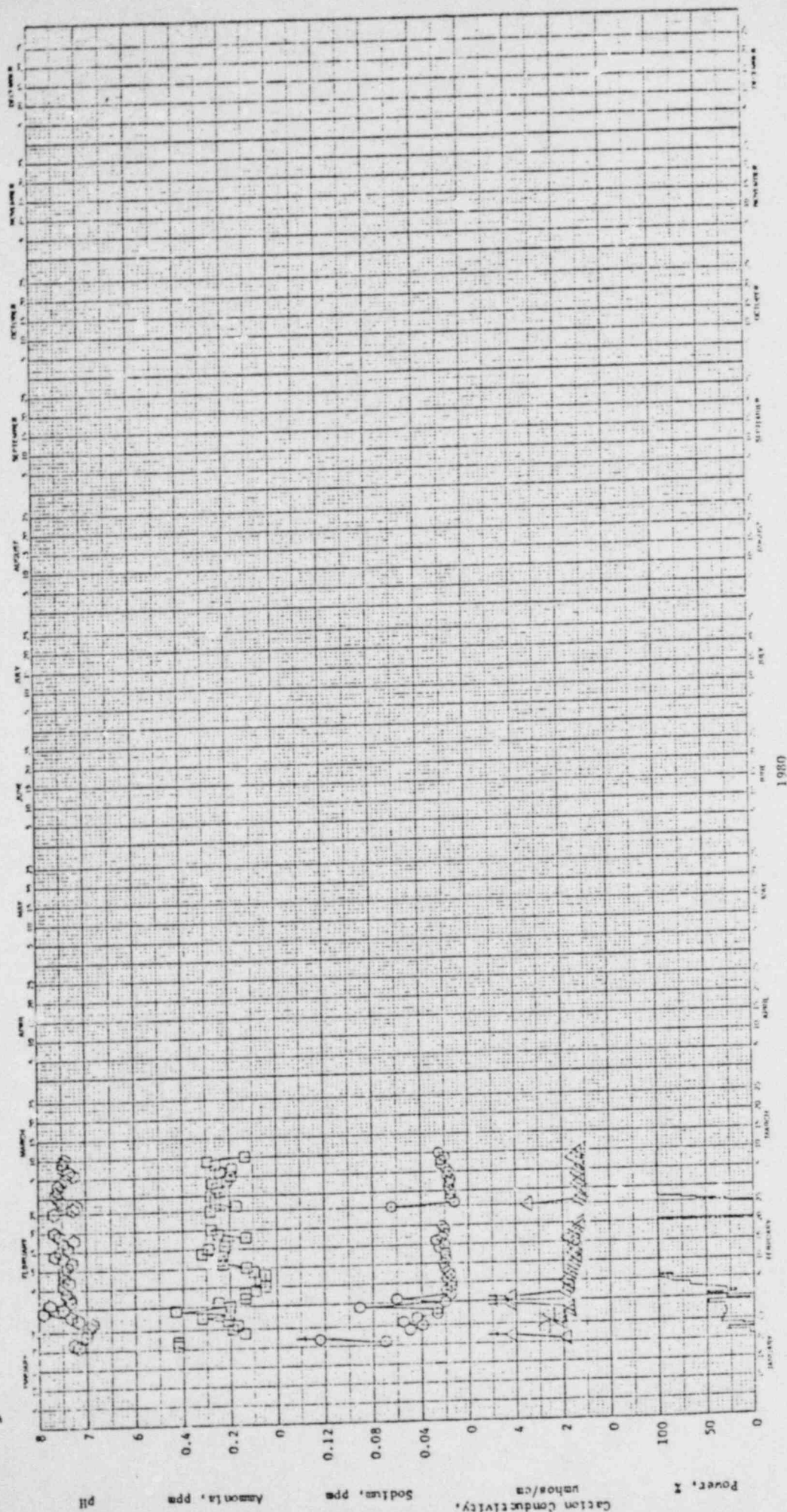


Figure 2C. Steam Generator A Blowdown Chemistry

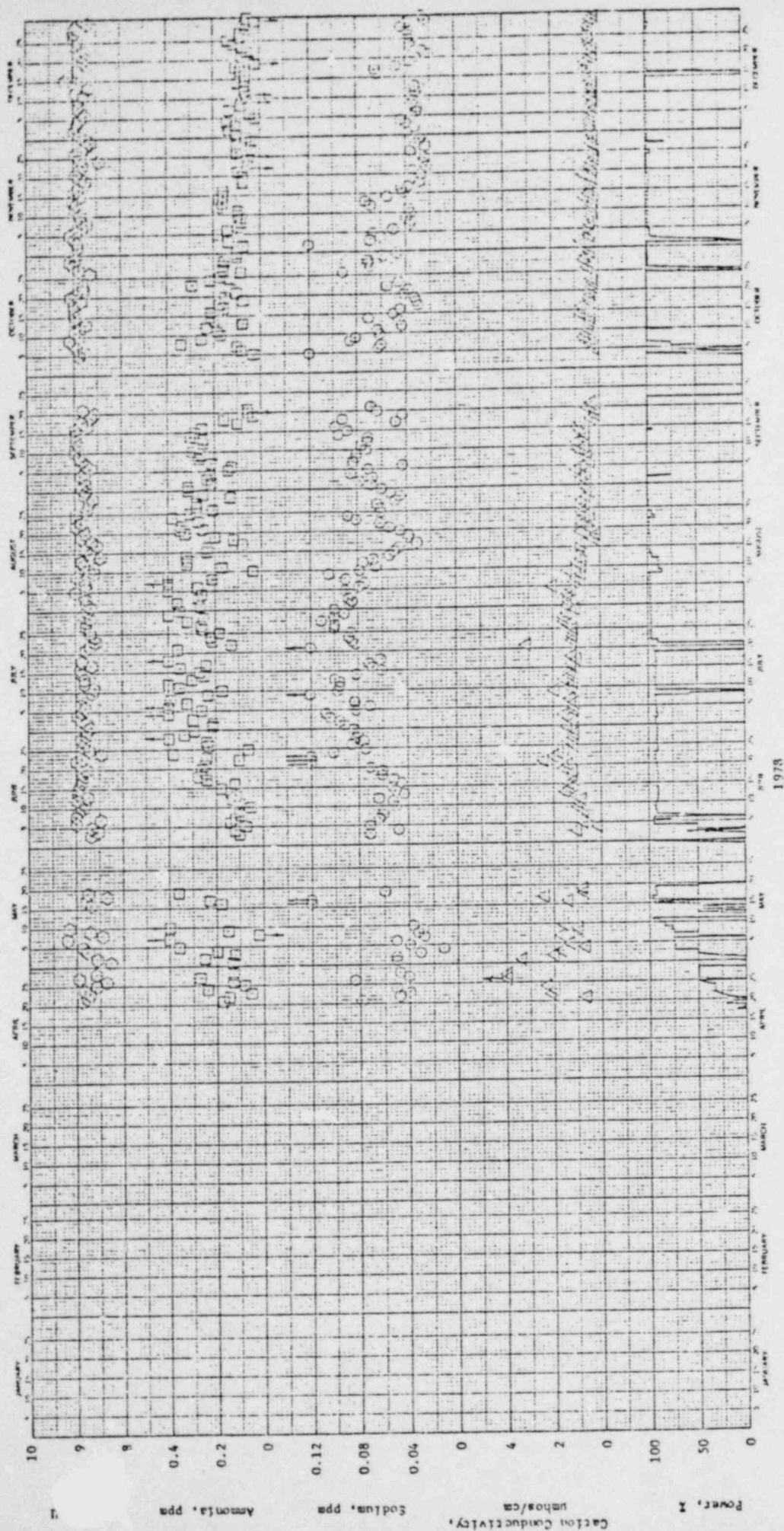


Figure 3A. Steam Generator B Blowdown Chemistry

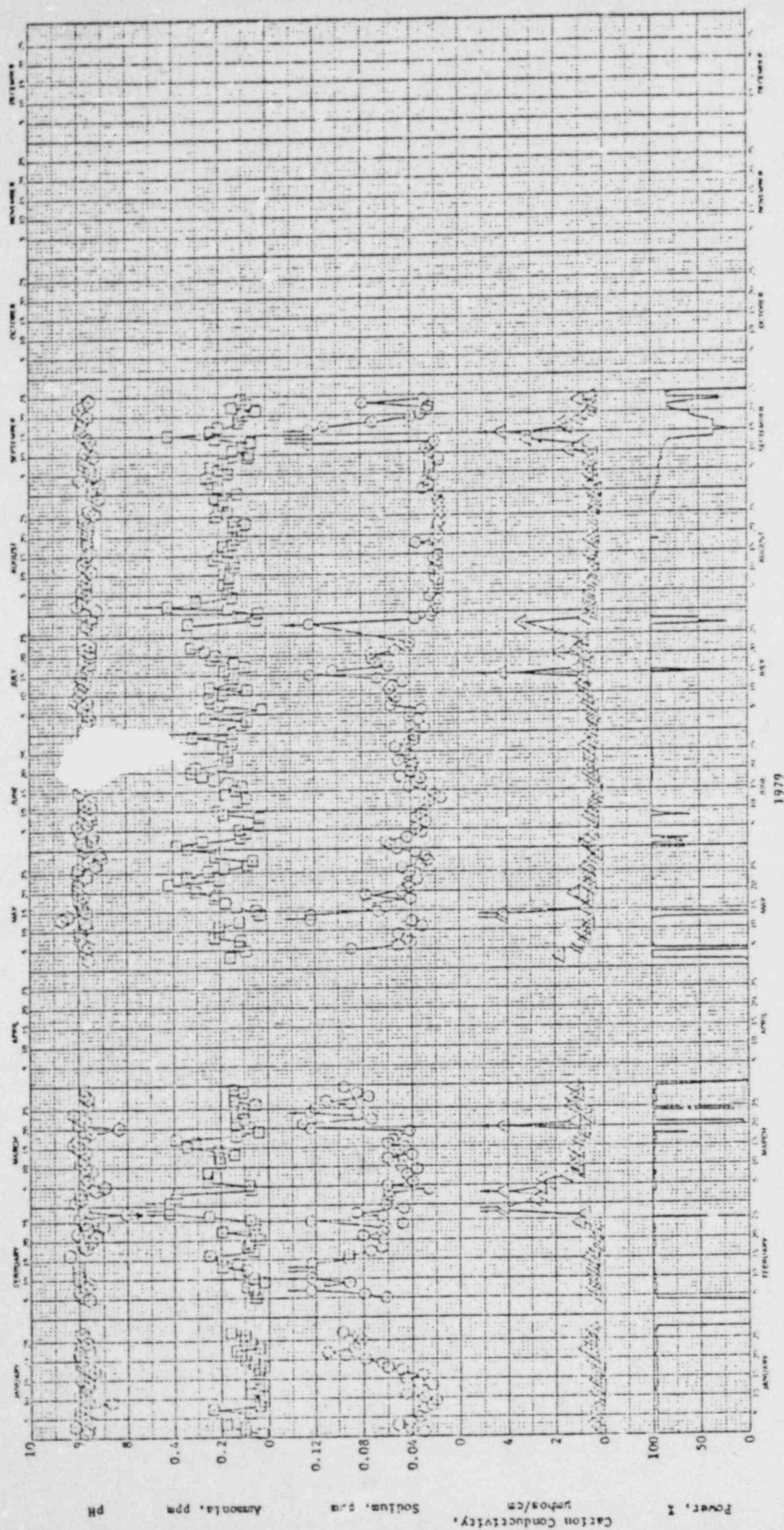


Figure 3B. Steam Generator B Blowdown Chemistry

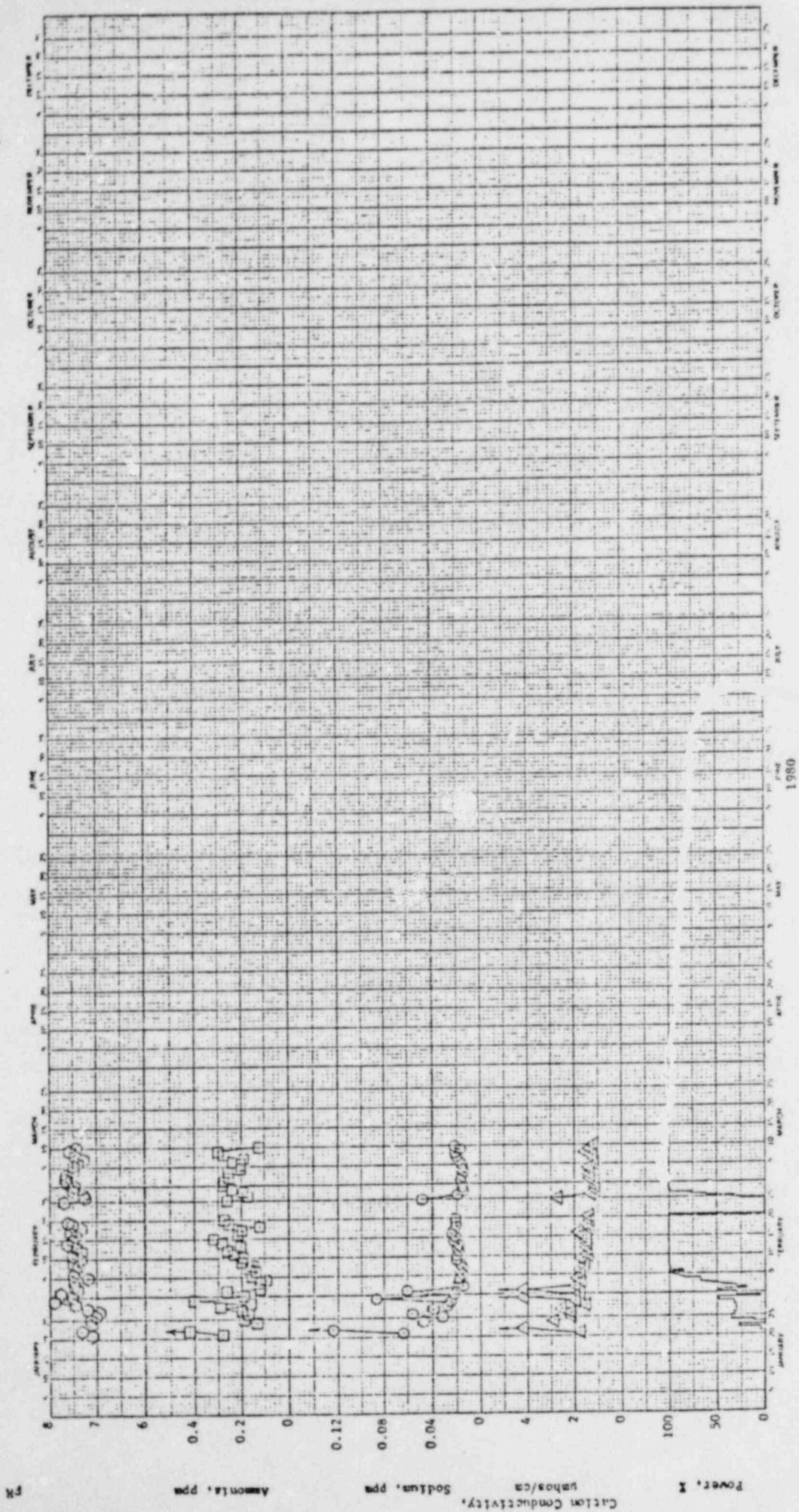


Figure 3C. Steam Generator Blowdown Chemistry

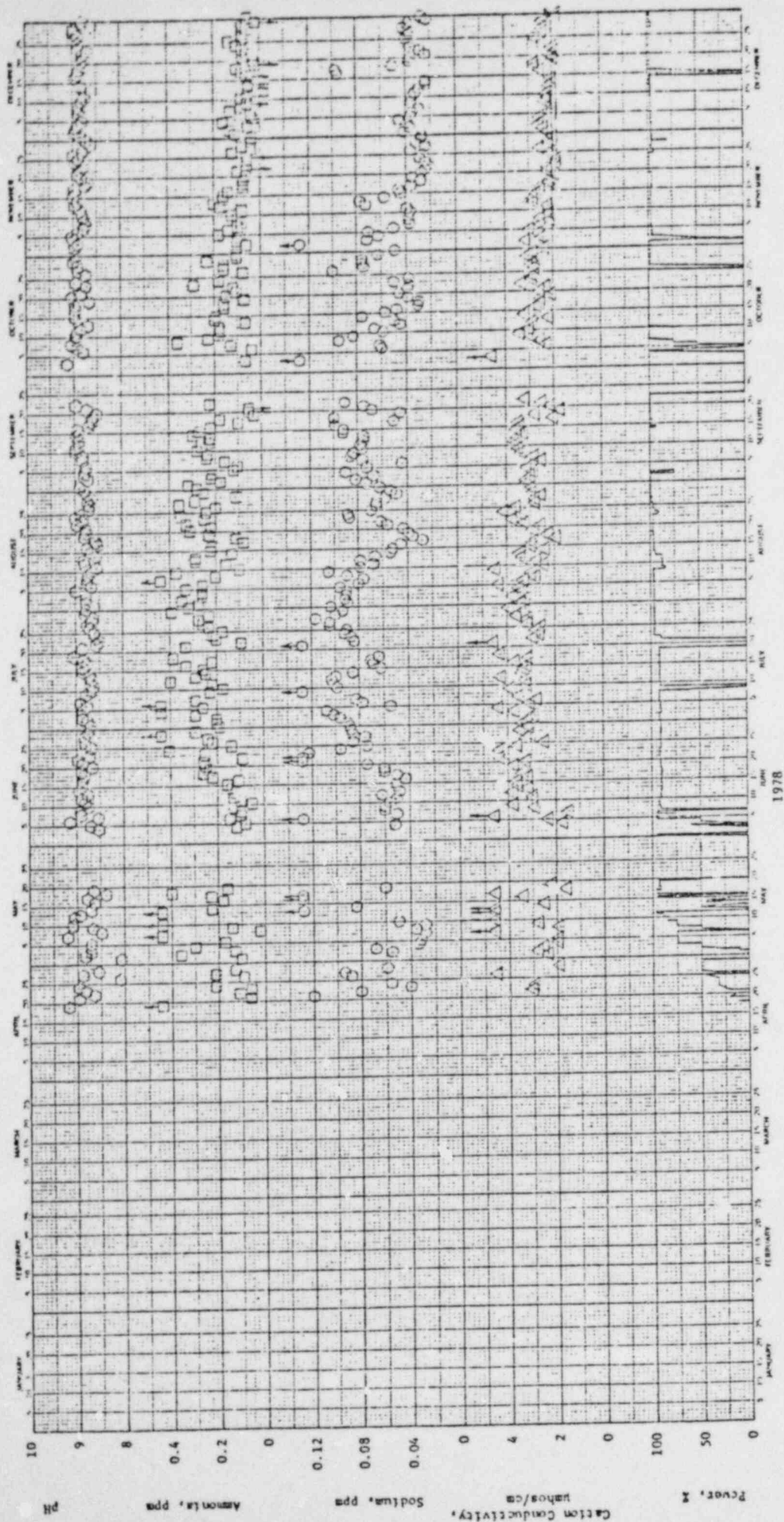


Figure 4A. Steam Generator C Blowdown Chemistry

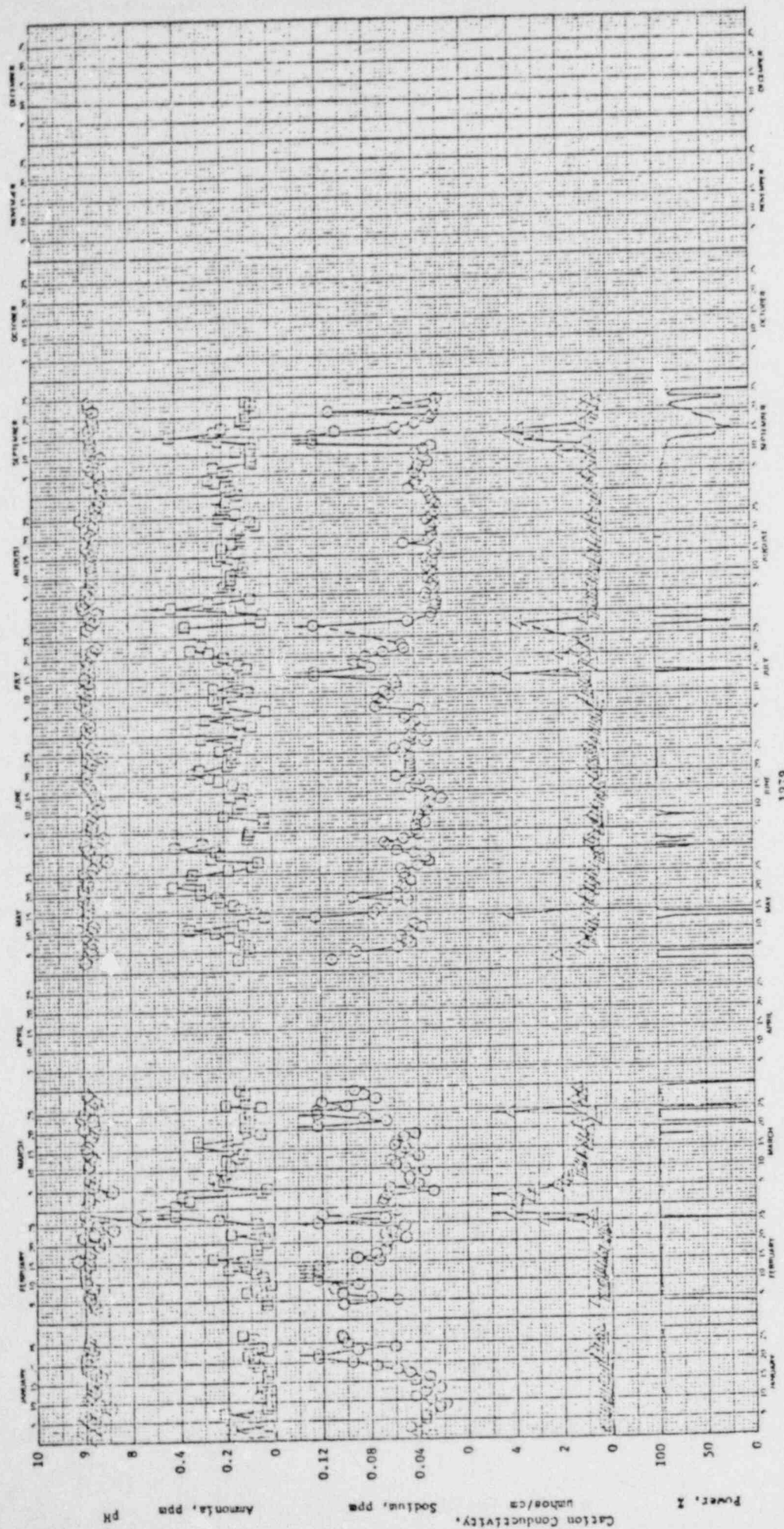


Figure 4B. Steam Generator C Blowdown Chemistry

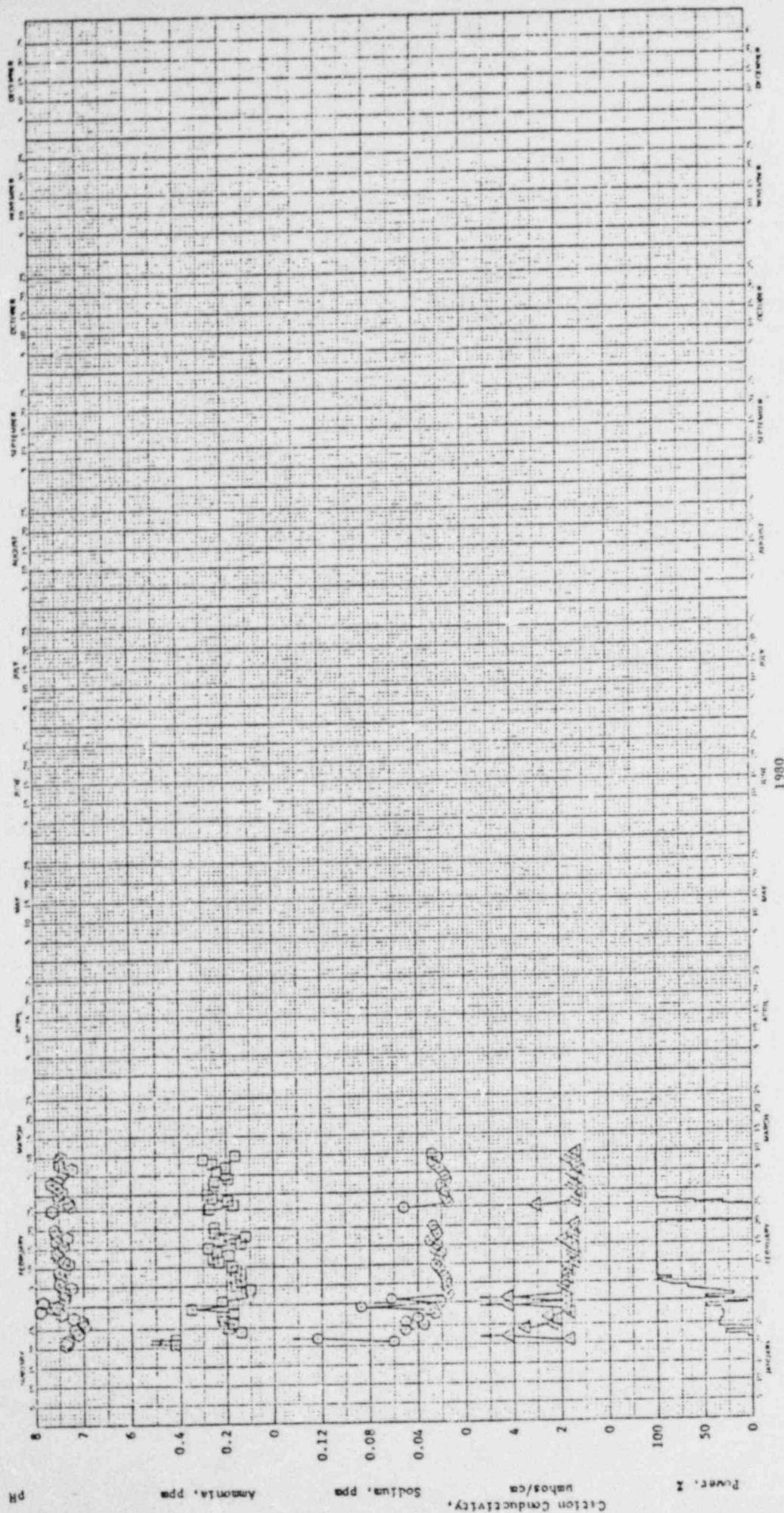


Figure 4C. Steam Generator C Blowdown Chemistry



have occurred (for example between May 5 and 10, 1978). However, there did not appear to be any significant resin intrusion as evidenced by a cation conductivity increase concurrent with a blowdown pH decrease (in the absence of a power transient). On an overall basis, chemistry variations appeared to reflect a gradual though long term cleanup. As a result of condenser cooling water inleakage, relatively simultaneous increases in sodium concentration and cation conductivity with a negligible pH change would be expected particularly during power transients. Several such chemistry transients occurred during 1978.

In 1979, blowdown chemistry transients became considerably clearer with respect to probable cause. If one focuses on interpreting the chemistry transients which could be associated with resin ingress, the transients in late February to early March, mid March, mid May, mid July, late July and mid September warrant consideration because of the significant cation conductivity increases above normal levels. Therefore, a review of these transients was undertaken.

During the chemistry transient on February 27 (Figure 5), blowdown cation conductivity increased to approximately 25 $\mu\text{mhos/cm}$ concurrent with a pH depression to 6 even though ammonia concentration was increased. There was a negligible change in sodium concentration associated with this incident. This transient clearly is associated with a resin intrusion, the extent of which is discussed below in more detail. On February 25 immediately prior to this incident, a simultaneous increase in sodium concentration and cation conductivity occurred with a negligible blowdown pH change. This transient was associated with the power reduction on February 25; it does not evidence the characteristic blowdown chemistry response to a resin intrusion. On March 24, a similar transient occurred (Figure 6), i.e., cation conductivity increased to approximately 5 $\mu\text{mhos/cm}$ with a concurrent sodium concentration increase to approximately 350 ppb. No significant change in steam generator pH or ammonia concentration occurred. The magnitude of the sodium and cation conductivity increases were similar to those observed during the February 25 power reduction before the major resin intrusion of February 27.

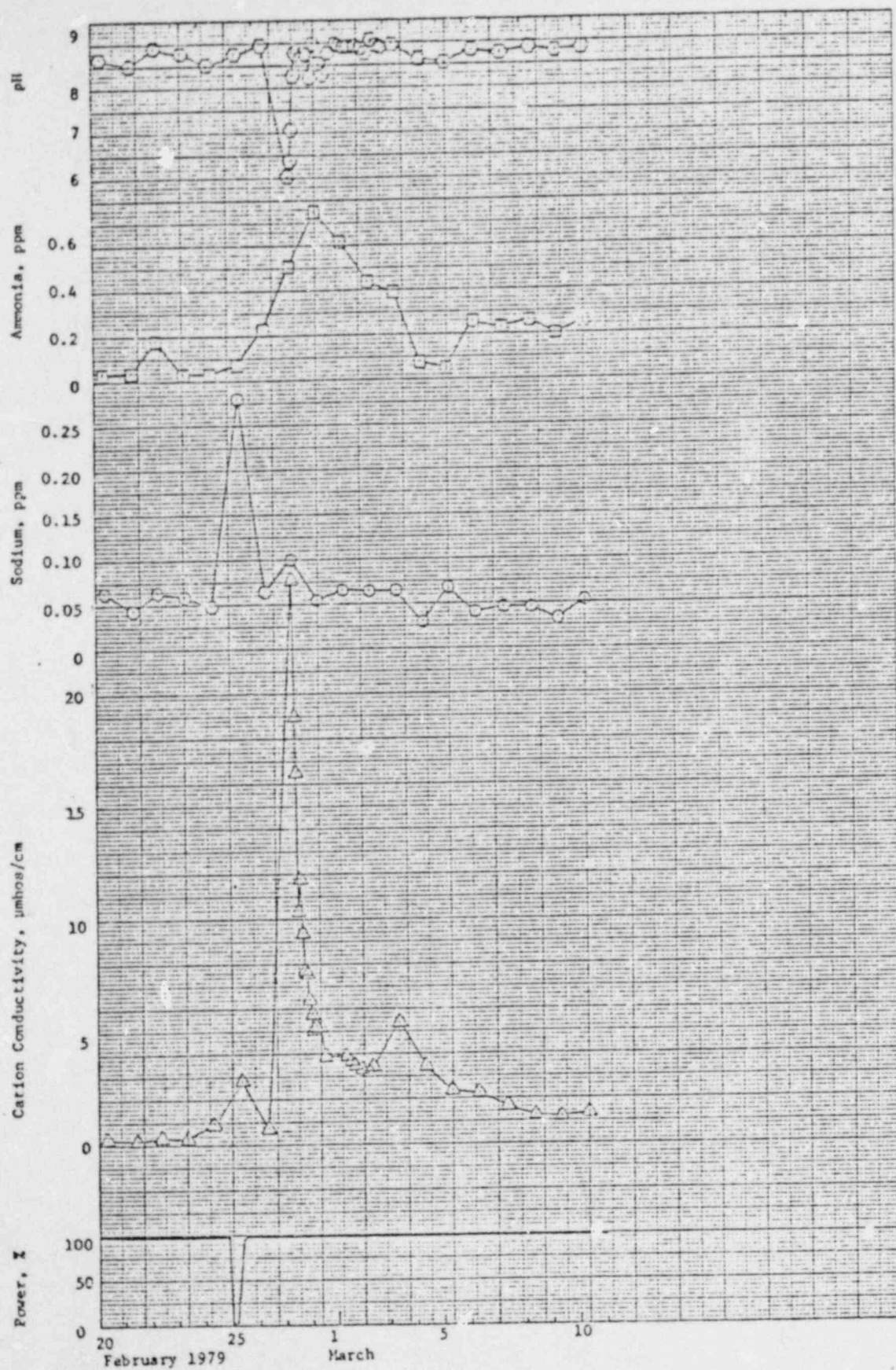


Figure 5. Steam Generator A Blowdown Chemistry (February-March 1979)

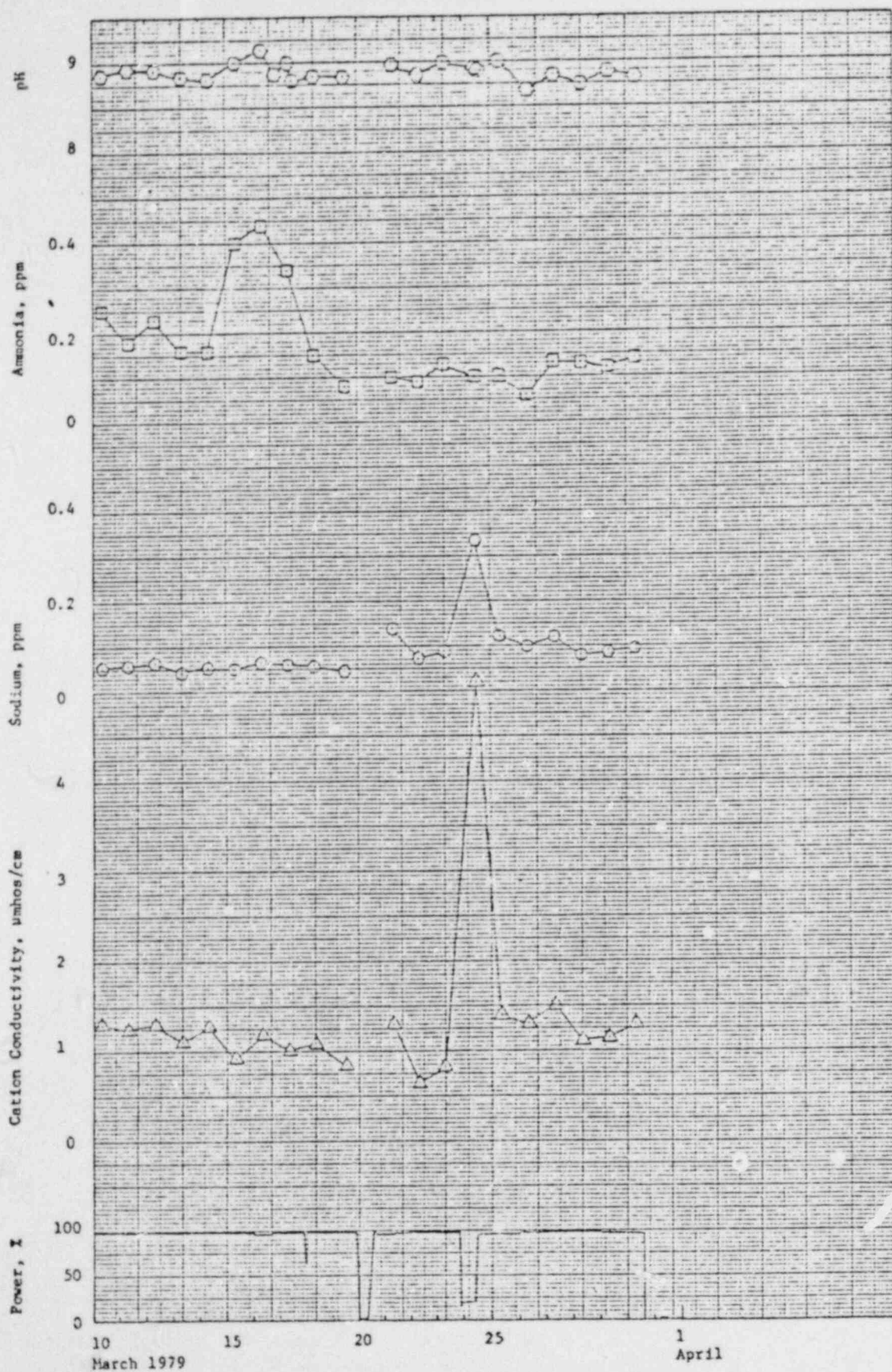


Figure 6. Steam Generator A Blowdown Chemistry (March-April 1979)



In early and mid May (Figure 7), simultaneous increases of sodium concentration and cation conductivity occurred during plant startup after short duration shutdowns. Again, these incidents appear to be associated with a shutdown/startup transient and the return of chemicals from hideout. Similarly, blowdown chemistry transients on July 15 and July 27 to 28 exhibit the characteristics of chemical return as a result of a power transient (Figure 8). They do not appear to be associated with resin intrusion. The transient on July 19 to 20 (and possibly July 25) exhibits the characteristics of a resin intrusion, i.e., an increase in cation conductivity without a concurrent increase in sodium. That ingress did occur is supported by comments in the plant logs: "D and E vessels broken due to high ΔP from excess resin".

In September 1979, several chemistry transients were associated with plant power variations (Figure 9). However, on September 10, an increase in cation conductivity occurred with a pH depression of approximately 0.3 units. Since no sodium increase was observed, this behavior appears to be associated with resin intrusion. That a minor resin intrusion did occur is supported by the plant logs: "Powdex vessel damage when placed in service". With a subsequent power reduction to below 80%, cation conductivity and sodium levels increased simultaneously without any significant change in blowdown pH. This transient (September 12-17) reflects chemical return from local regions in the steam generator.

Based on the available chemistry data, it does not appear that any other significant resin intrusion incidents occurred during 1979 or 1980 (through March 10).

In submittals to the NRC, three minor resin intrusions into the steam generator following the February 27 intrusion were reported as having occurred. This observation is consistent with the result of our review if it can be accepted that the July 25 transient was associated with an intrusion.

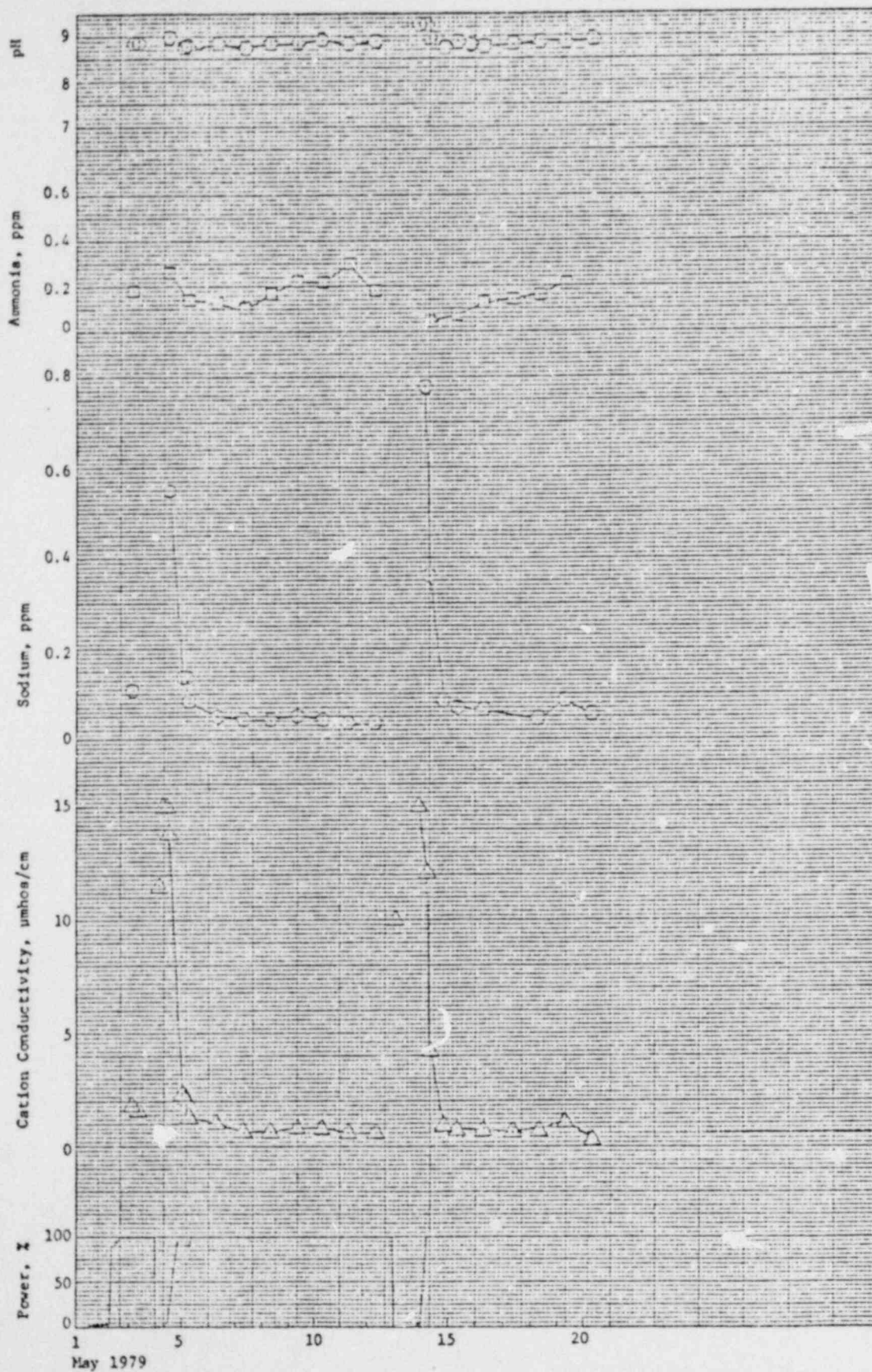


Figure 7. Steam Generator A Blowdown Chemistry (May 1979)

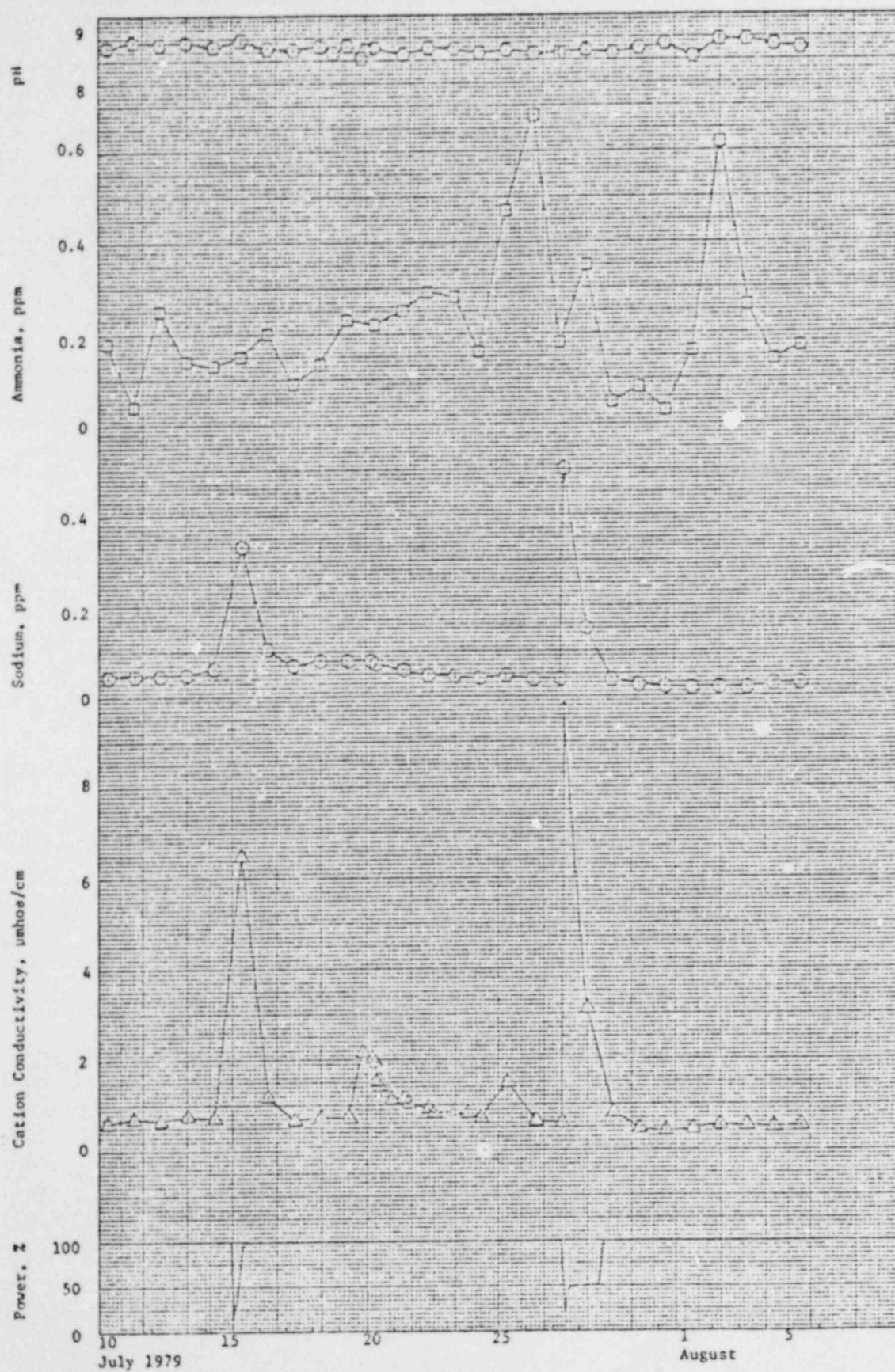
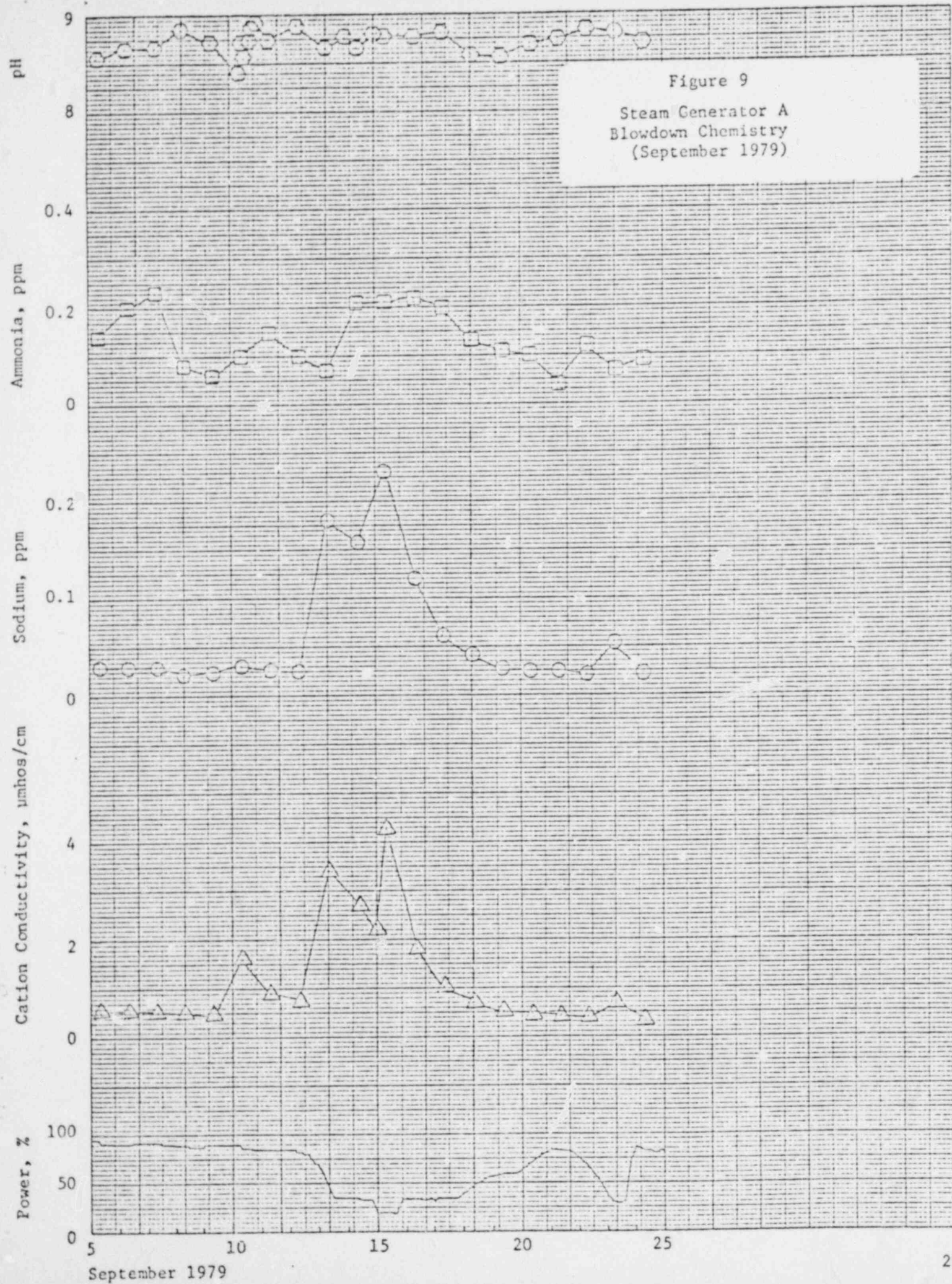


Figure 8. Steam Generator A Blowdown Chemistry (July-August 1979)





To estimate the quantity of resin which entered the steam generators on February 27, it was assumed that all of the cation resin was in the hydrogen form, and decomposition proceeded totally to formation of sulfate. With this assumption, the total amount of sulfate removed from the steam generator by blowdown can be employed to calculate the amount of cation resin that entered the generators. From the variation in cation conductivity, the sulfate concentration can be estimated as shown in Figure 10. In the absence of a balancing cation, the maximum sulfate concentration in the generator would give a room temperature pH of approximately 4. This predicted pH is significantly lower than the value of 6 reported by plant personnel during the incident. This leads the authors to conclude that the resin intrusion incident occurred rapidly enough that steam volatilization of balancing cations was not sufficiently rapid to allow the full pH transient to be experienced in the bulk coolant. However, lower pH levels probably occurred in local areas where concentration factors above that in the steam generator coolant are much greater than those in the bulk.

Based on the blowdown sulfate concentration variation, the total sulfate removal by blowdown was approximately 17 pounds (Figure 11). This corresponds to cation resin ingress on the order of 44 pounds (dry). Corresponding anion resin ingress (C:A = 3:1 precoat) is 14 pounds (dry). The total resin ingress estimate of 58 pounds is somewhat lower than that previously reported to the NRC¹ (technique unknown). Based on the ratio of maximum cation conductivity during resin intrusions on July 10, July 21 and September 10 to that on February 27, resin ingress during these three incidents was estimated to be 3, 1 and 2 dry pounds, respectively.

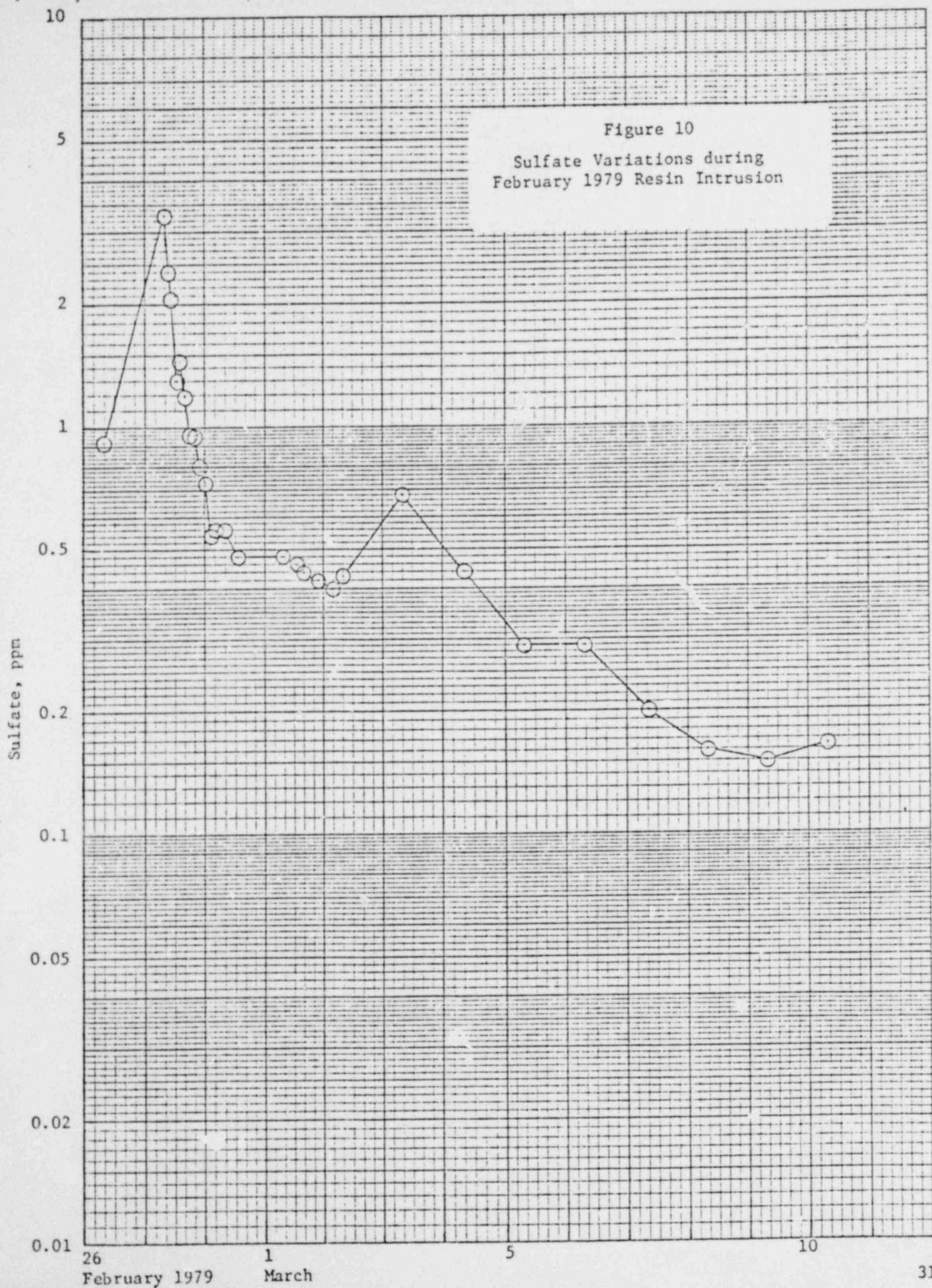
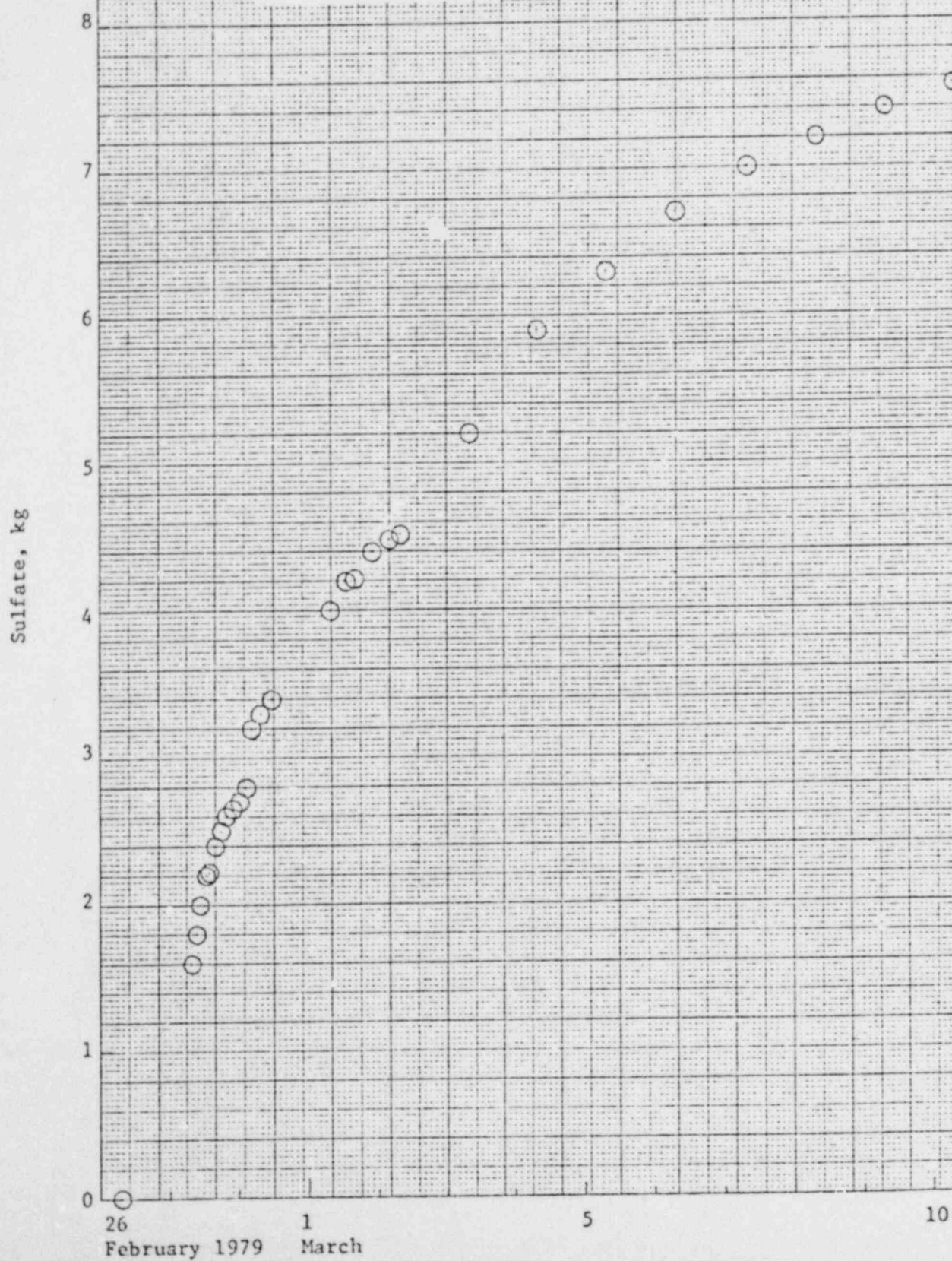


Figure 11
Sulfate Removal from System
during February 1979
Resin Intrusion





EFFECTS OF LAKE COOLING WATER INGRESS

Lake Anna cooling water chemistry was employed in the NWT model on crevice chemistry in PWR steam generators to assess effects of condenser inleakage. Lake water leakage rate was adjusted to give a 100 ppb blowdown sulfate level. As shown in Figure 12, lake water ingress in the absence of condensate polishing would be expected to increase crevice pH, i.e., basic not acid solutions would be formed. Unfortunately, detailed ionic removal efficiency data for the North Anna powdered resin filters were not available thus the effect the polisher has on each ionic species could not be considered in the analysis. Nonetheless, it appears unlikely that acid forming solutions could be formed during lake water ingress even if the effect of the powdered resin filters were considered.

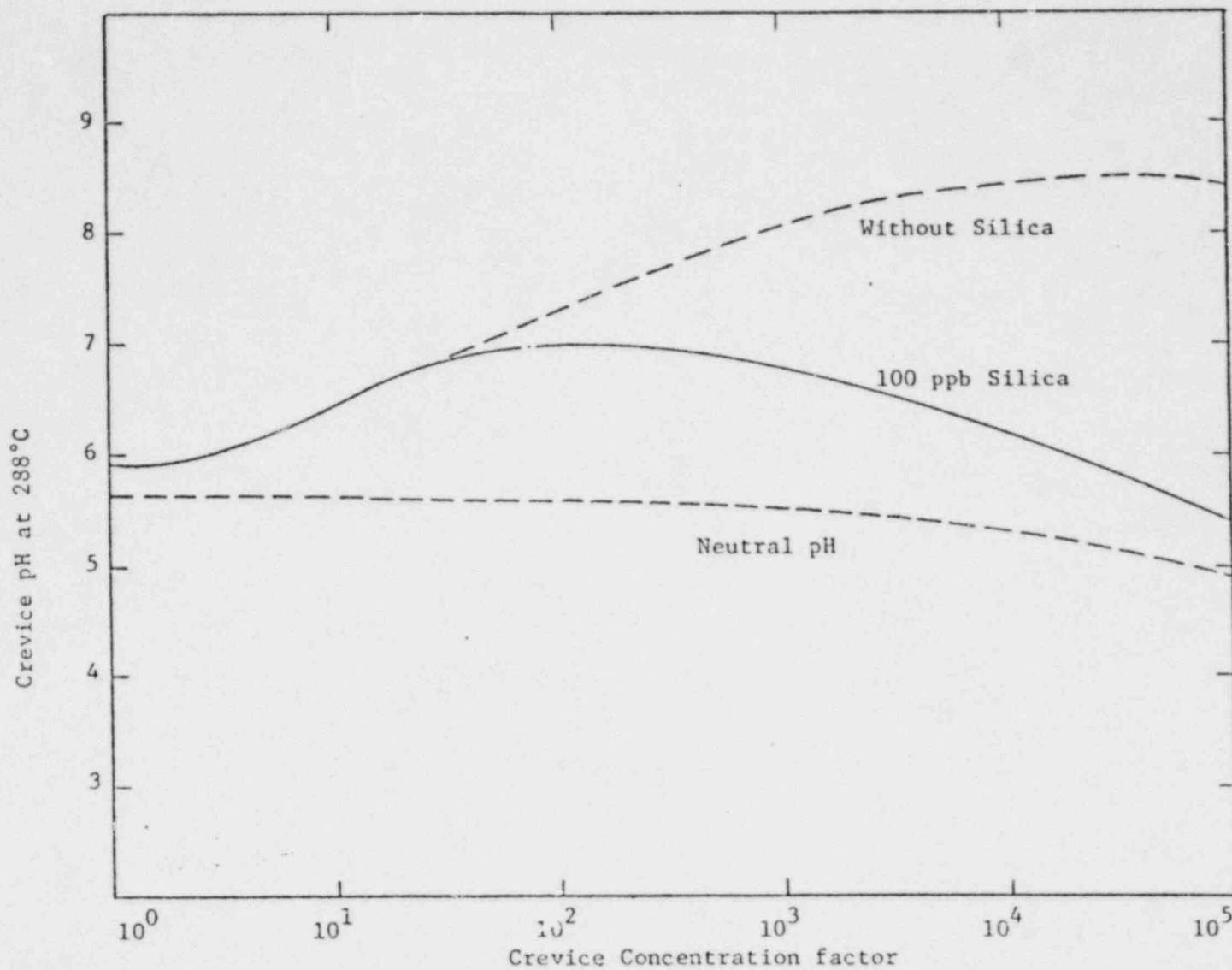


Figure 12. Variation of Crevice pH during Condenser Leakage (Blowdown Sulfate = 100 ppb)



DISCUSSION

Steam generator blowdown chemistry other than during the resin intrusion of February 27, 1979 appears to have been controlled reasonably. However, average cation conductivity and sodium levels particularly during 1978 were much higher than expected considering the high quality cooling water, the full-flow condensate polishing system, and the high capacity blowdown system. Although not abnormal with respect to the overall response to a power transient, chemical return during plant startups and shutdowns before and subsequent to the resin intrusion exhibits a distorted sodium to anion ratio, i.e., sodium return is higher than expected. This enrichment of sodium return could be resulting from continued low level condenser leakage with preferential sodium leakage through the condensate filters (as expected) or sodium input from fresh precoat material as a result of a fraction of the new resin being in the sodium form. In any event, the anion return (sulfate or chloride) evidenced by the cation conductivity increases does not appear higher than that expected to be associated with the sodium increase in the absence of resin decomposition products. This infers that these decomposition products were removed from the generators as they decomposed. This position is consistent with the following Westinghouse sludge analysis results:²

"Microscopic examination of the sludge showed its physical appearance to be similar to other plant sludges with no distinguishing characteristics. The carbon analyses in each sample was in the range of the carbon content of sludge from plants without condensate polishing units. Also, the sulfate concentration in each sample was similar to that found in sludge from plants without condensate polishing."

Only limited studies have been made on the effect of resin intrusion on steam generator corrosion. The most thorough program to date has been performed by Combustion Engineering (CE) for EPRI.

In Phase 1 of EPRI RP623-1 performed by CE, cation resins (sodium form) and anion resins (chloride form) were injected intermittently into a 16 tube model boiler, and the extent of Alloy 600 and carbon steel attack assessed. Average model boiler chemistry is given in Table 8.³



TABLE 8
MEAN SECONDARY CHEMISTRY VALUES - PHASE 1

pH @ 25°C	8.9
Specific conductivity	22 μ mhos/cm
Intensified conductivity	47 μ mhos/cm
Sodium	1.5 ppm
Chloride	0.8 ppm
Sulfate	2.0 ppm
Sulfite	1.0 ppm

Model boiler chemistry variations are shown in Figure 13 for the last 2½ months of the test. As shown, the model boiler underwent several chemistry transients as severe as the major transient at North Anna 1. Combustion Engineering summarized their corrosion observations from this phase of the program as follows:³

"After 94 days of steaming, the unit was shut down and opened for an interim examination. ECT was performed on all heat transfer tubes at 100 and 400 kHz. No indications of any corrosive degradation was noted on the tubing. Visually, the tube surfaces were coated with a thin adherent dull grey oxide, which subsequently was analyzed to be Fe_3O_4 . On top of the magnetite film was an intermittent layer of mustard-yellow resin fines. Resin fines appeared sporadically on the carbon steel internals and shrouding material."

The model exposure was continued for an additional 182 days in Phase 2. Resin injections were continued, and chemistry transients were considerably more severe (reference Figure 14 for "typical month"). Average monthly conditions are given in Table 9. After this additional exposure, observations were as follows:³

"The final examination of this model was performed after an additional 182 steaming days (276 days total). At this time, ECT indicated tube denting at all locations within the carbon steel drilled support plate and in the tubesheet crevices for those tubes which were not installed by explosive expanding. The maximum radial constriction at the support (as measured by ECT) was 0.0165" with an average radial dent of 0.011"

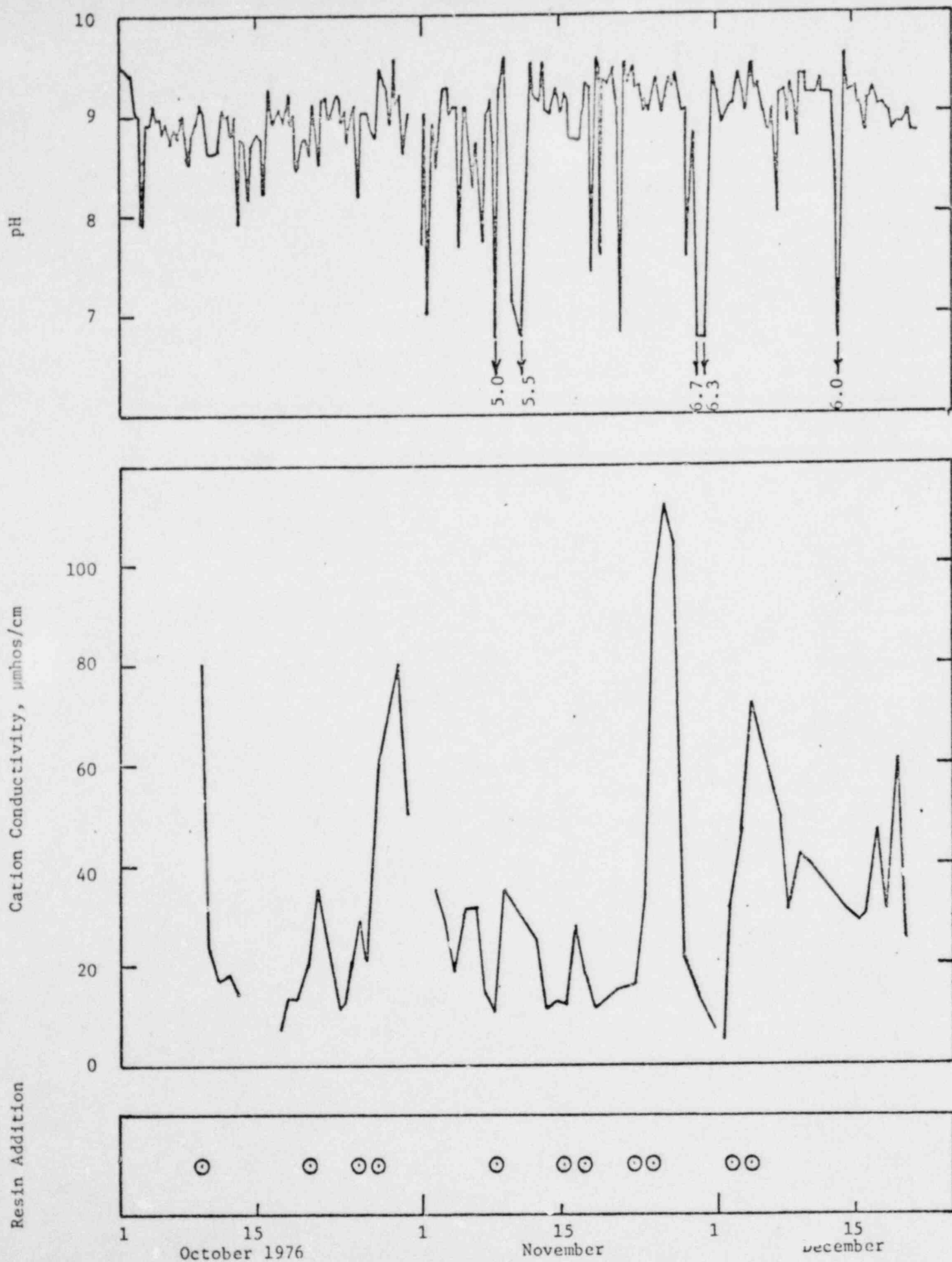


Figure 13. RP623-1 Phase 1 Chemistry (Combustion Engineering)

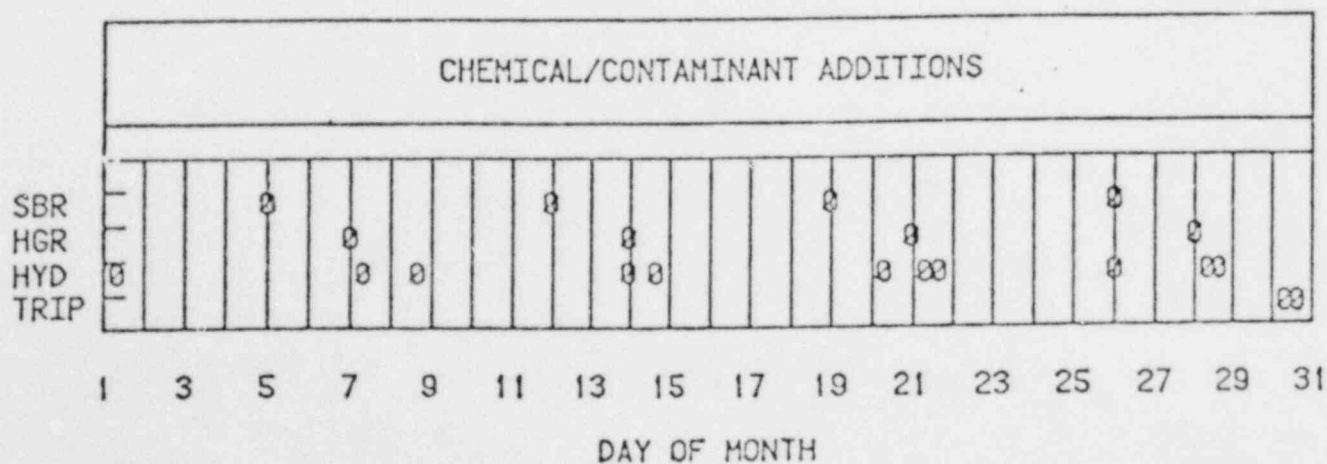
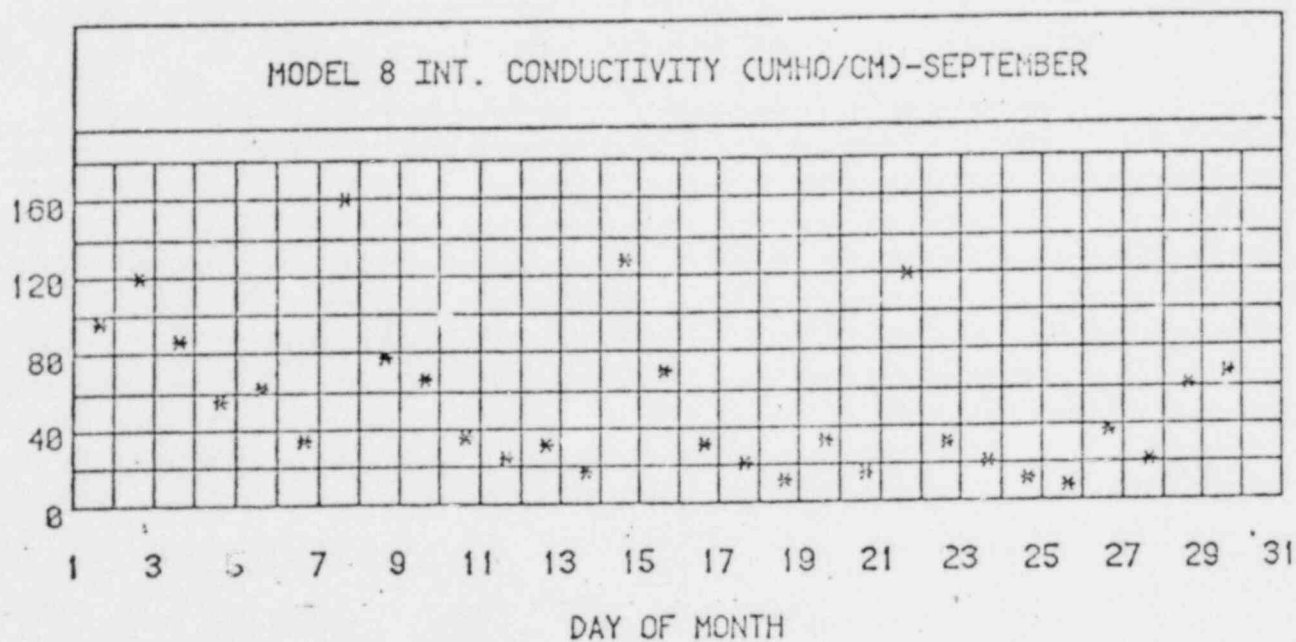
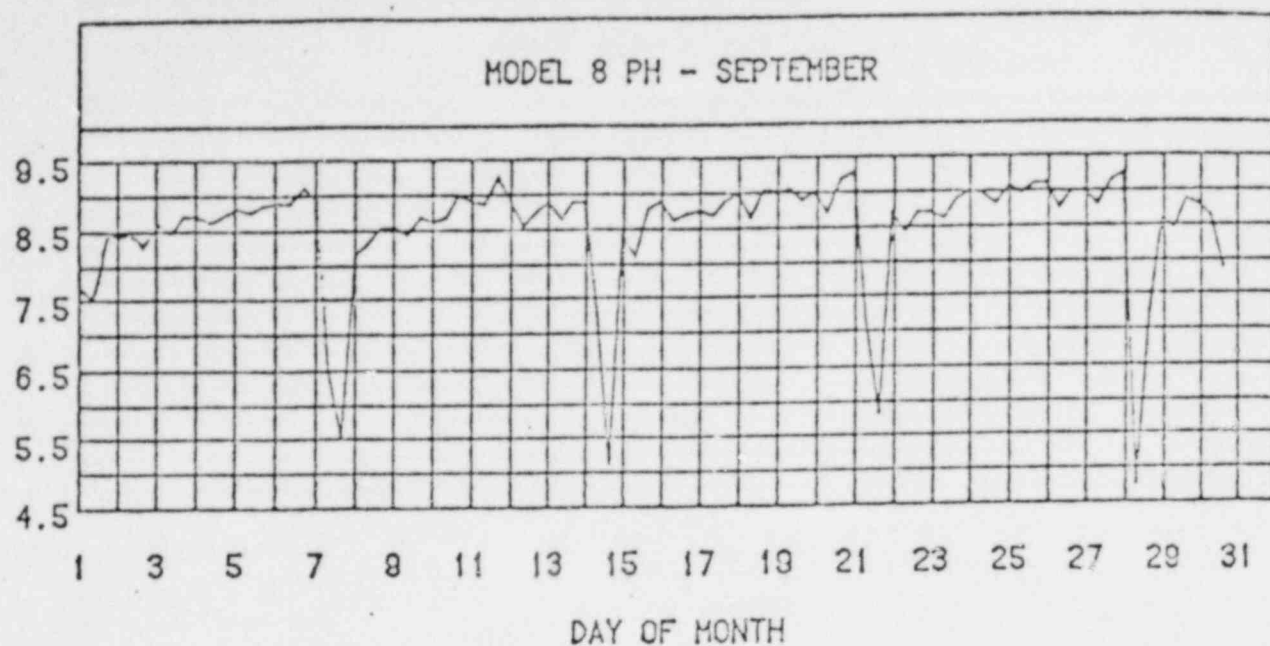


Figure 14. Typical RP623-1 Phase 2 Chemistry (Combustion Engineering)

TABLE 9
MEAN SECONDARY CHEMISTRY VALUES - PHASE 2

<u>Date</u>	<u>pH</u>	<u>(μmho/cm)</u>		<u>ppm</u>				
		<u>S.C.*</u>	<u>I.C.**</u>	<u>Na</u>	<u>Cl</u>	<u>S***</u>	<u>NH₃</u>	<u>SiO₂</u>
4/77	8.8	14.0	--	0.3	0.15	--	--	0.2
5/77	9.0	22.5	49.5	1.2	1.2	2.9	1.9	0.2
6/77	8.6	24.5	55.4	1.5	1.7	4.5	1.6	0.1
7/77	8.8	23.0	43.5	1.5	0.9	4.3	2.1	0.1
8/77	8.5	28.1	75.4	2.1	1.2	9.8	2.9	0.2
9/77	8.6	24.9	54.0	1.7	0.5	10.3	2.4	0.1
10/77	8.6	13.7	16.4	0.5	0.26	3.0	1.5	0.2
11/77	8.6	10.2	10.6	0.05	0.10	2.3	1.7	0.1

*Specific conductivity

**Cation conductivity

***Total sulfur as sulfate



for the 32 tube/plate insertions. At the tubesheet, the average radial constriction was approximately 0.004". Also, ECT indicated approximately 20% wall thickness loss for several tubes in the steam blanketed U-bend region..."

"Samples of the tubesheet sludge were obtained at model shutdown and analyzed by x-ray diffraction and fluorescence. The diffraction pattern indicated that magnetite was the major species although the pattern showed other unidentifiable species.... Note that in addition to Fe and Cu, substantial quantities of C were found. This is probably the result of thermal decomposition of the organic resin structure. Other elements, whose concentration was found to be greater than 0.5% (by weight), were Mn and Ni; Cr and S were detected in concentrations greater than 0.4%."

Since in Phase 1 of RP623-1 aggressive tube support plate corrosion was not experienced in the model boiler, it became difficult for the authors to accept that the single incident at North Anna 1 could have led to "denting" and possible ligament cracking. However, although the model boiler chemistry perturbations and normal chemistry appear more severe than at North Anna 1, the model boiler heat flux was much lower. This difference could explain the apparently more rapid attack at North Anna.

As the final step in the evaluation, more quantitative estimates of the attack magnitude at North Anna were sought. Unfortunately, available documentation did not specify average dent size or range. Discussions with Vepco personnel also did not allow estimates to be developed. In some instances, the presence of "only minor support plate corrosion" was indicated.¹ In other references,⁴ full blown denting is indicated to be present, and North Anna is listed in a table with Indian Point 3, Kori I, etc. This classification appears questionable since only one tube restricted passage of the 0.700-inch ECT probe at North Anna whereas several hundred such tubes were detected at Indian Point 3 during their second inspection.⁵ Clarification of the magnitude of the attack will be required before further assessments relative to the relation of the resin intrusion incidents to the attack can be quantified.



RECOMMENDATIONS

The following actions are recommended for Vepco consideration:

1. Develop and/or make available quantitative estimates of dent magnitude at each intersection based on ECT records. The authors recognize the inaccuracy of the ECT technique for dent magnitude assessment, however, even semiquantitative estimates would be of value.
2. Characterize blowdown chemistry at North Anna during current boric acid injection program. Blowdown samples during steady and transient conditions should be collected and submitted to NWT for analysis for Na, Ca, Mg, Cl, and SO_4 .
3. Transient and steady state effects of powdered resin filter insertion and long term operation of one vessel should be determined. Condensate, demineralized condensate, moisture separator drain, feedwater and blowdown levels of the above 5 species should be determined for several weeks during which one or more powdered resin precoated filters are put into operation.
4. Routine operation of the resin filters should not be reinitiated until resin strainers are installed, and appropriate interlocks are provided to prevent future occurrence of premature filter valving into the system. Adequacy of operator training also should be assessed.



REFERENCES

1. Stallings, C. M., Virginia Electric & Power Company, letter to H. R. Denton, Nuclear Regulatory Commission, December 10, 1979.
2. Douth, V. W., Westinghouse Electric Corporation, letter to B. R. Sylvia, Virginia Electric & Power Company, January 22, 1980.
3. Baldwin, M. H., et al., "C-E/EPRI Program RP-623-1, PWR Model U-Tubed Steam Generator Corrosion Studies, Fourth Progress Report", Combustion Engineering, July 1979.
4. London, R. S., Westinghouse Electric Corporation, letter to C. M. Stallings, Virginia Electric & Power Company, November 27, 1979.
5. "Attachment III, Safety Evaluation related to Steam Generator Inspections", Power Authority of the State of New York, Indian Point 3 Nuclear Plant, January 1980.



APPENDIX A¹

"POWDEX RESIN DISCHARGED INTO STEAM GENERATORS"

"On February 27, 1979, while placing a Powdex vessel in the condensate polishing system back into service, the filter tubes were ruptured allowing the Powdex resin to be carried to the steam generators. The exact quantity of resin discharged to the steam generators is not known, but is estimated to be 200 to 300 pounds.

"The operational events leading to the discharge hinge on the timing of fill and pressurize operations on a single Powdex vessel during return to service following installation of a new resin charge. Normally, after the filter elements are coated with resin, the vessel is slowly filled and pressurized to establish flow through the filter elements. The operating pressure differential across the filter elements is established as the discharge-side pressure follows the inlet-side pressure up to operating pressure. Thus, when the main condensate inlet line is opened, admitting condensate at operating pressure (~400 psig), a controlled ΔP across the filter elements has already been established.

"During this event, however, the condensate inlet line opened before the vessel had been completely filled and an operating ΔP had been established across the filter elements. This surge of higher pressure condensate created an abnormally high ΔP across the filter elements, rupturing the element seals. This permitted condensate to carry the resin off the filter elements and out through the vessel discharge valve."



APPENDIX B²

"STEAM GENERATOR CHEMISTRY SUMMARY"

"A review of plant chemistry data logs was performed to investigate the cause of the steam generator corrosion. The discharge of Powdex resin into the steam generator on February 27, 1979, caused chemistry parameter excursions as shown in the table below:

Steam Generator Chemistry Parameters Before and After Resin Discharge Event

	<u>Baseline</u>	<u>Immediate Effect</u>
pH @ 25°C	8.8-9.0	6.02
Cation Conductivity	<0.4 μ mhos	25 μ mhos
Chloride	<0.05 ppm	0.05 ppm (unchanged)
Sodium	<0.04 ppm	0.1 ppm
Silica	<0.1 ppm	0.33 ppm
Ammonia	<0.2 ppm	0.59 ppm

The long term effects of the resin discharge on steam generator chemistry were as follows:

1. Cation conductivity returned to less than 2 μ mhos on March 7, 1979. This is the first time since the discharge on February 27, 1979, that this parameter was within recommended limits.
2. Load reductions and shutdowns have caused cation conductivity excursions to as high as 40 μ mhos (5-2-79).
3. Steam generator chemistry approached baseline values toward the end of May 1979.

The major findings of a Westinghouse review of plant chemistry data logs are as follows:

1. Reported anions, cations, and cation conductivities are not in balance.
2. Sodium concentration consistently exceeds that required for chloride stoichiometry.
3. Cation excursions not due to chlorides.
4. A large anion inventory exists in the steam generators and evidence indicates that this is due to sulphates.
5. Numerous events of silica passing through the Powdex system due to resin saturation have occurred. Silica in condensate results from condenser inleakage."