

# DUKE POWER COMPANY

POWER BUILDING

422 SOUTH CHURCH STREET, CHARLOTTE, N. C. 28242

WILLIAM O. PARKER, JR.  
VICE PRESIDENT  
STEAM PRODUCTION

April 29, 1982

TELEPHONE: AREA 704  
373-4083

Mr. Harold R. Denton, Director  
Office of Nuclear Reactor Regulation  
U. S. Nuclear Regulatory Commission  
Washington, D. C. 20555

Attention: Ms. E. G. Adensam, Chief  
Licensing Branch No. 4

Re: Catawba Nuclear Station  
Docket Nos. 50-413 and 50-414



Dear Mr. Denton:

Elinor G. Adensam's letter of October 22, 1981 transmitted question 282.1 from the Corrosion Engineering Section of the Chemical Engineering Branch. Our response is provided in the attached revision to FSAR Section 10.3.5.2, which will be included in a future FSAR Amendment. Also attached is a copy of the PWR Secondary Water Chemistry Guidelines (September 1981) which is referenced in the revised Section 10.3.5.2.

Very truly yours,

A handwritten signature in dark ink, appearing to read "William O. Parker, Jr.", written over the typed name.

William O. Parker, Jr.

ROS/php  
Attachment

cc: Mr. James P. O'Reilly  
Mr. P. K. Van Doorn  
Mr. R. Guild  
Palmetto Alliance  
Mr. J. L. Riley  
Mr. H. Presler

Boo1  
S/1

CNS

282.0

CORROSION ENGINEERING

282.1  
(10.3.5)

The secondary water chemistry monitoring and control program as you provided in the FSAR is incomplete. Provide a complete secondary water chemistry monitoring and control program following the guidance of Branch Technical Position MTEB 5-3 attached to SRP 5.4.2.1, Revision 2, July 1981.

Response:

See revised Section 10.3.5.2.

Station chemistry procedures will be available for on-site review at least six months prior to fuel load.

## CNS

by station operating personnel. See Section 6.2.4.4 and the Inservice Pump and Valve Testing Program (per ASME Section XI, IWP/IWV) for the testing and inspection of the main steam isolation valves.

### 10.3.5 WATER CHEMISTRY

#### 10.3.5.1 Effect of Water Chemistry on the Radioactive Iodine Partition Coefficient

As a result of the basicity of the secondary side water, the radioiodine partition coefficients for both the steam generator and the air ejector system are decreased (i.e., a greater portion of radioiodine remains in the liquid phase). However, the lack of data on the exact iodine species and concentrations present prevents a quantitative determination of the coefficient decrease for these systems. The partition coefficients used for site boundary dose calculations are those given in NUREG 0017. For the steam generators, a partition coefficient of 0.01 was used while for the main condenser air ejector the partition coefficients used were 0.15 for volatile iodine species and zero for non-volatile species, assuming 5% of the iodine species are volatile.

#### 10.3.5.2 Secondary Side Water Chemistry

Water purity in the secondary system, and in the steam generators in particular, is maintained within specified limits in order to minimize corrosion and to minimize fouling of steam generator heat transfer surfaces.

##### 10.3.5.2.1 Treatment

All volatile treatment (AVT) is provided by the chemical addition of hydrazine for oxygen scavenging and ammonia for maintaining pH.

In addition, powdered resin demineralizers are used for condensate polishing, and an air removal section in the condenser is used to remove oxygen from the feedwater.

##### 10.3.5.2.2 Monitoring

Samples are collected from the steam generators, condensate and feedwater. Instrumentation is provided to monitor pH, conductivity, silica, hydrazine, sodium, and oxygen. As a minimum, the guidelines proposed in the PWR Secondary Water Chemistry Guidelines (September 1981), Chapter 2 - Recirculating Steam Generators will be met for point of monitoring and frequency of monitoring.

##### Q281.1 10.3.5.2.3 Controlling Chemistry

Operating the polishing demineralizers properly and maintaining condenser vacuum will control the quality of feedwater. In addition, blowdown of the steam generators is used to maintain chemistry limits. The chemistry guidelines proposed in the PWR Secondary Water Chemistry Guidelines (September 1981), Chapter 2 - Recirculating Steam Generators will be used as the controlling chemistry criteria. High purity makeup water (Specifications Table 10.3.5-2) and chemical additives are added as needed.

PWR SECONDARY WATER CHEMISTRY GUIDELINES

September 1981

Prepared by:

Steam Generator Owners Group  
Water Chemistry Guidelines Committee

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## RECIRCULATING STEAM GENERATORS

### 2.1 Overview

#### 2.1.1 Introduction and Scope

These guidelines reflect current understanding of the role of chemical transport, impurity concentrations, material selection, corrosion behavior, chemical analysis methods and industry practices on the operation and integrity of steam generator systems.

The criteria for the establishment of the guideline parameters were:

1. Ingress of impurities to the steam generator is to be kept to a practical and achievable minimum.
2. Impurity concentrations are maximum values consistent with the currently known corrosion behavior of steam generator and secondary system materials.
3. Impurity concentrations are detectable by currently available equipment and procedures.

Using these criteria, guidelines have been formulated which provide chemistry control while retaining operating flexibility. These guidelines describe parameters to be measured and provide normal and action level values. The normal values are based in part on proven plant experience with minimal impurity ingress and corrosion. Wherever possible, literature sources and the results of research in progress are cited to justify the parameter values. As more data become available, added justification for some parameter values will be provided.

Typical corrective actions are recommended in several sections in this chapter. These corrective actions are not meant to be all inclusive or universally applicable and should be modified for plant-specific concerns.



Action levels and their impact upon plant operation are discussed in Section 2.1.2. The three plant status modes (cold shutdown, hot standby and power) covered by these guidelines are discussed in Section 2.1.3.

These chemistry limits and action levels are considered to be minimum requirements for protection against secondary system and steam generator corrosion in plants using ammonia-hydrazine treatment. These guidelines are applicable for any cooling water source and are consistent with the philosophy that plants should be operated with the lowest practicable impurity levels consistent with their circumstances. These guidelines do not cover transient operation or transition from one operating mode to another (e.g., hot standby to power). These guidelines also do not cover alternative water chemistries such as boric acid treatment.

The tables of parameters give values for individual chemical species and water conditions. However, it is realized that the steam generator water system represents a complex equilibria between a large number of interdependent variables. The values of oxygen and pH will effect copper and iron, the sum of all anions will effect cation conductivity, blowdown values are related to feedwater values, the sodium level should be balanced against chloride and sulfate to avoid excess acidity or alkalinity, etc. The list of interactions is long and generally not quantifiable. Existing data are inadequate for the consideration of these interactions in detail; however, they are covered as far as the data permits and should be considered in the development of specific guidelines for the individual plants.

It is recognized that some water chemistry values, monitoring techniques and corrective measures being recommended may require additional equipment in some plants. In addition to the monitoring recommendations of Section 2.1.4, plants should consider additional continuous monitors (e.g., cation conductivity or sodium in each condenser hot well, etc.) to assist in the detection of abnormal chemistries (see Chapter 4).

### 2.1.2 Action Levels

Three action levels have been defined for taking remedial action when monitored parameters are observed and confirmed to be outside the normal operating value. Normal operating value as it is used here refers to the value of a parameter which is consistent with long-term system reliability. Action Level 1 is implemented whenever an out-of-normal value is detected. The normal values given for Action Level 1 are practical and achievable in the field. Although exceeding the normal values will not necessarily result in a proven corrosive condition, maintaining parameter values within the normal range will provide a high degree of assurance that corrosive conditions will be avoided. Action Level 2 is instituted when conditions exist which have been shown to result in some degree of steam generator corrosion during extended full (100%) power operation. Action Level 3 is implemented when conditions exist which will result in rapid steam generator corrosion and continued operation is not advisable.

#### Action Level 1

Objective: To promptly identify and correct the cause of an out-of-normal value without power reduction.

#### Actions:

- a) return parameter to within normal value range within one week following confirmation of excursion
- b) if parameter is not within normal value range within one week following confirmation of excursion go to Action Level 2 for those parameters having Action Level 2 values

#### Action Level 2

Objective: To minimize corrosion by operating at reduced power while corrective actions are taken. Power reduction should be to a level which will reduce available steam generator superheat and heat flux while providing



sufficient system flow to maintain automatic operation while the source of the impurity is corrected. This reduced power level is typically 30% of full power or less.

Actions:

- a) reduce power to appropriate level (typically 30% or less) within four hours of initiation of Action Level 2
- b) return parameter to within normal value range within 100 hours or go to Action Level 3 for those parameters having Action Level 3 values

Action Level 3

Objective: To correct a condition which may result in rapid steam generator corrosion during continued operation. Plant shutdown will avoid ingress and eliminate further concentration of harmful impurities.

Actions:

- a) shut down within four hours and clean up by feed and bleed or drain and refill as appropriate until normal values are reached

Typical Corrective Actions

When a parameter has reached an action level value, corrective actions should be implemented. These corrective actions will be parameter and plant specific. Each plant should have a predefined course of action which has been developed with attention to specific concerns. The following actions may be considered typical:

- a) increase steam generator blowdown to maximum levels for removal of specific impurities,
- b) compare results of confirmatory analyses to readings from continuous monitors,

- c) compare results of various analyses for internal consistency,
- d) increase sample and analysis frequencies for short-term trending of critical chemistry parameters, and
- e) isolate and identify sources of impurity ingress.

### 2.1.3 Status Modes

The steam generator status modes covered in these guidelines are:

1. Cold Shutdown
2. Hot Standby
3. Power

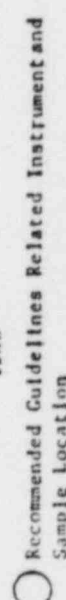
Cold Shutdown: The steam generator should be placed in wet layup with chemically treated water whenever practical during outages to minimize surface corrosion. During power reduction prior to shutdown, steam generator bulk water will contain significant levels of impurities from hideout return. The cold shutdown period should be used to reduce this impurity inventory by feed and bleed, flushing, or drain and refill.

Hot Standby: During hot standby the steam generator is ready for steaming operation. This period should be used to reduce impurity inventories in the steam generator in preparation for power operation.

Power: Because the steam generator is most susceptible to corrosion from impurity ingress while at power, the monitoring procedures and normal values cited are the most rigorous of any mode. Action Level 2 and 3 values are provided for several critical parameters during power operation.

### 2.1.4 Sample Sources

Figure 2-1 shows recommended instrument and sample point arrays for the blow-down, feedwater and condensate in a recirculating steam generator system. Auxiliary feedwater should be sampled at a point which will provide a



2-5

representative sample. Sample points shown in circles are consistent with guideline recommendations for monitoring. Those enclosed in squares are recommended for diagnostic measurements to aid in the detection and location of impurity ingress. Sample points and recommended instrumentation are discussed in Chapter 4.

## 2.2 Cold Shutdown

### 2.2.1 Introduction

Wet layup of the steam generators (and the feedwater train, if practical) during outages with chemically treated water is desirable to minimize surface corrosion. Protection is provided by an ammonia-hydrazine solution which is based on both fossil fuel boiler experience and on laboratory studies [1].\* These studies show that proper layup chemistry can provide corrosion protection for six months or longer.

To provide for mixing of the bulk solution during cold shutdown, nitrogen sparging and/or recirculation are necessary. A positive nitrogen overpressure should be maintained during filling, draining, and cold shutdown to minimize oxygen ingress. Flushing procedures to reduce the inventory of steam generator impurities should be considered at this time. These procedures have been developed and employed at several plants and have been proven effective in reducing impurities.

Mixing of steam generator bulk solution and adequate sample line flush times provide chemistry samples which are representative of steam generator contents. The steam generator bulk solution should be mixed and sampled every other day (after parameters are in the normal range) until the parameters are stable, then weekly.

If copper alloys are present in the system, excess hydrazine should be discharged prior to startup to prevent thermal decomposition to ammonia. Ammonia at high concentrations can cause copper alloy corrosion.

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\*Numbers in brackets [ ] indicate references listed in Section 2.5.

Special attention should be given to the auxiliary feedwater since it can represent a significant source of oxygen ingress to the system. The guideline values presented in Table 2-1b are ambitious; however, efforts should be made to approach these goals as closely as practicable so as to control this source of oxygen.

Prior to heating to hot standby, steam generator chemistry parameters should be in the range of hot standby guidelines (see Section 2.3).

The guideline parameters for cold shutdown are given in Table 2-1, the justifications are discussed in Section 2.2.3, and typical corrective actions are given in Section 2.2.4.

#### 2.2.2 Tables of Parameters and Values

Table 2-1a

##### RECIRCULATING STEAM GENERATOR COLD SHUTDOWN BLOWDOWN SAMPLE

<u>Parameter</u>	<u>Frequency*</u>	<u>Normal Value</u>	<u>Initiate Action</u>	<u>Value Prior to Heatup</u>
pH (ferrous system)	3/week	9.8-10.5	<9.8, >10.5	>9.0
pH (ferrous/copper system)	3/week	9.8-10.5	<9.8, >10.5	8.5-9.2
Hydrazine, ppm	3/week	75-200	<75, >200	--
Sodium, ppb	3/week	<1000	>1000	<100
Cation Conductivity, μmho/cm	3/week	<10.0	>10.0	<2.0

\* Every other day until stable, then weekly.

Table 2-1b

RECIRCULATING STEAM GENERATOR  
COLD SHUTDOWN  
AUXILIARY FEEDWATER SAMPLE

<u>Parameter</u>	<u>Frequency</u>	<u>Normal Value</u>	<u>Initiate Action</u>
Dissolved O <sub>2</sub> , ppb	3/day	<100 in fill	>100 in fill

### 2.2.3 Justification for Parameters and Values

pH: Hydrazine solutions in the pH range of 9.8-10.5 provide corrosion protection for steam generator materials through the formation and maintenance of a protective film [2]. In systems having copper alloys the pH must be reduced to 8.5-9.2 prior to heat-up to avoid corrosion of these components.

Hydrazine: Hydrazine is an oxygen scavenger and inhibits general and localized corrosion of ferrous materials [1]. The hydrazine concentration should be maintained between 75 and 200 ppm. Hydrazine solutions with a pH greater than 9.8 enhance the formation of a protective magnetite film on the metal surface.

Sodium: Sodium is maintained below 1000 ppb to ensure that contaminants are maintained at acceptable levels prior to startup. If sodium levels exceed 1000 ppb, steam generators should be drained and refilled.

Cation Conductivity: Cation conductivity is intended as a check on total anionic impurities in the steam generator. Cation conductivity can be compared with chloride (see Figure 2-2) as a preliminary check on internal consistency. The cation conductivity guideline of <10.0  $\mu\text{mho/cm}$  will assist in achieving good water quality prior to heat-up.

Dissolved Oxygen: Dissolved oxygen increases the corrosion rate of iron surfaces [1]. The oxygen concentration should be below 100 ppb in the fill and makeup water to minimize these effects.



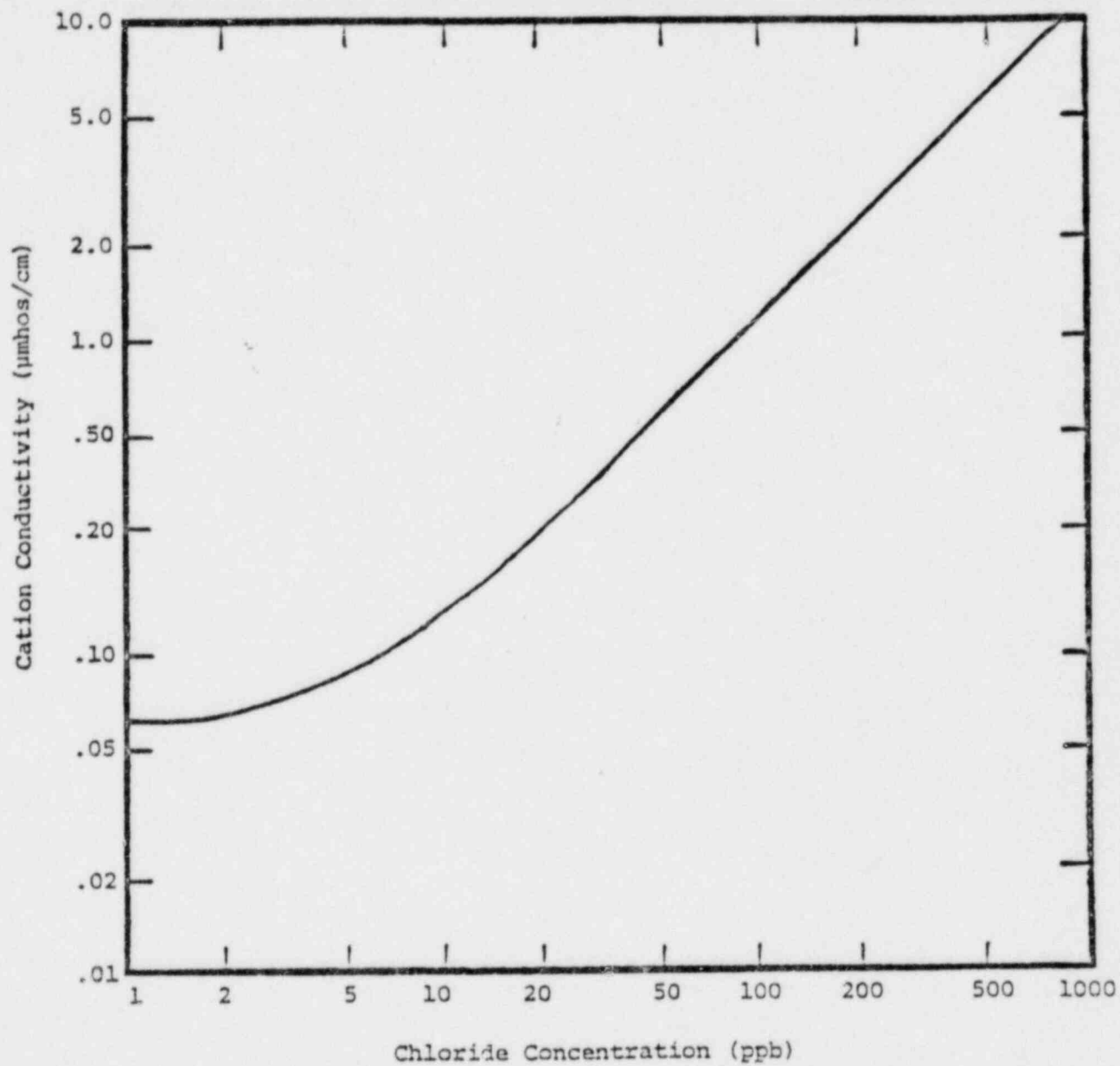


Figure 2-2. CHLORIDE CONCENTRATION VS. CATION CONDUCTIVITY  
AT 25°C IN THE ABSENCE OF OTHER ANIONIC SPECIES

A nitrogen blanket should be maintained at a slight positive pressure (e.g., 5 psi) to eliminate oxygen ingress during cold shutdown [3,4]. When the steam generators are drained, a nitrogen cover should be maintained if possible. Concerns for exposure of personnel to local oxygen deficient environments during maintenance may require special precautions and interruption in nitrogen supply. After maintenance is completed, the steam generator should be refilled with ammonia-hydrazine solution and a nitrogen blanket reestablished.

#### 2.2.4 Corrective Action Guidelines - Cold Shutdown

##### Parameter Out of Range

##### Corrective Action

pH

1. Cross-check with ammonia/hydrazine/cation conductivity values for consistency.
2. If low, add ammonia to correct and mix contents of steam generator.
3. If high, feed and bleed or drain and refill with makeup water of the proper purity.

Hydrazine

1. If low, add until within range.
2. If high, with copper condenser or copper feed system, drain and refill to reduce concentration prior to heat-up.

Sodium

1. Check makeup water purity.
2. Feed and bleed or drain and refill with deoxygenated makeup water of proper purity.

Cation Conductivity

1. Feed and bleed or drain and refill with deoxygenated makeup water of proper purity.

#### 2.3 Hot Standby

##### 2.3.1 Introduction

The period between cold shutdown and hot standby should be used to reduce impurity levels in the steam generator, achieve hot standby parameter values, and prepare for power operation. During hot standby, feed and bleed (makeup and blowdown) is the only method available for reducing impurity levels.

During hot standby, sampling of steam generator auxiliary feedwater (at the condensate storage tank) and blowdown are required (see Section 2.1.4 for sample sources). Feedwater parameters (Table 2-2a) were selected to ensure that water of good quality was being supplied. Primary consideration was given to oxygen and hydrazine levels. Blowdown parameters (Table 2-2b) were selected to maintain water chemistry of adequate quality for power operation. Maintenance of good water quality at this time will reduce the impact of hideout during power escalation.

Care must be taken to avoid the overaddition of hydrazine (with the resultant decomposition to ammonia) to mixed ferrous/copper systems which have an upper pH limit.

Steam generator blowdown chemistry should be below Action Level 2 guideline values for power operation (Table 2-3b) before starting power escalation, and below Action Level 1 guideline values before exceeding 30% power.

The guideline parameters for hot standby are given in Table 2-2 and justifications are discussed in Section 2.3.3. Guidelines for corrective actions are in Section 2.3.4.

### 2.3.2 Tables of Parameters and Values

Table 2-2a

RECIRCULATING STEAM GENERATOR  
HOT STANDBY  
AUXILIARY FEEDWATER SAMPLE

<u>Parameter</u>	<u>Frequency</u>	<u>Normal Value</u>	<u>Initiate Action</u>
Dissolved O <sub>2</sub> , ppb	daily	<100	>100
Hydrazine, ppb	daily	>3 x [O <sub>2</sub> ]	<3 x [O <sub>2</sub> ]

Table 2-2b

RECIRCULATING STEAM GENERATOR  
HOT STANDBY  
BLOWDOWN SAMPLE

<u>Parameter</u>	<u>Frequency</u>	<u>Normal Value</u>	<u>Initiate Action</u>	<u>Value Prior to Power Escalation</u>
pH (ferrous system)	continuous	>9.0	<9.0	—
pH (ferrous/copper system)	continuous	8.5-9.2	<8.5 >9.2	--
Cation Conductivity )mho/cm	continuous	<2.0	>2.0	<2.0
Dissolved O <sub>2</sub> , ppb	daily	<5	>5	—
Sodium, ppb	continuous	<100	>100	<100
Chloride, ppb	daily	<100	>100	<100

### 2.3.3 Justification for Parameters and Values

pH: The pH range depends upon the materials present in the feedtrain. For all ferrous systems the pH should be above 9.0, whereas for systems containing both ferrous and copper alloys, operation should be between 8.5 and 9.2. A minimum pH is specified to protect ferrous materials, and a maximum pH is specified to protect mixed ferrous and copper systems.

Cation Conductivity: Cation conductivity is used as an indicator of the total dissolved anions present. Its value should correspond to the total strong anion concentration obtained by other analytical procedures or the reason for the discrepancy should be determined.

Dissolved Oxygen: To minimize carbon steel corrosion oxygen ingress must be controlled. Dissolved oxygen in the auxiliary feedwater should be less than 100 ppb and should be treated with adequate hydrazine. Blowdown dissolved oxygen levels during hot standby should be less than detectable (<5 ppb by

colorimetric measurements). This can be achieved by control of oxygen in the makeup water.

Sodium: Sodium comes from condenser inleakage, makeup water or condensate polisher regenerant chemicals. Sodium hydroxide (caustic) is of major concern due to potential corrosion of turbine and steam generator tubing materials.

Chloride: Chloride promotes the growth of nonprotective magnetite in crevice regions (denting), promotes pitting attack, and is carried over to the turbine. Control of chloride is necessary under hot standby conditions to limit hideout during power escalation.

Hydrazine: To control oxygen in the auxiliary feedwater, hydrazine is maintained at a level of three times the feedwater oxygen. This should result in blowdown oxygen levels of  $\leq 5$  ppb.

#### 2.3.4 Corrective Action Guidelines - Hot Standby

##### Auxiliary Feedwater Parameter Out of Range

##### Corrective Action

Dissolved oxygen

1. Check hydrazine residual and add as required.
2. Check air inleakage.

Hydrazine

1. Add if residual is low.

##### Steam Generator Blowdown Parameter Out of Range

##### Corrective Action

pH

1. If low, adjust ammonia feed.
2. If high, blow down and add demineralized, deoxygenated makeup water.

Cation conductivity

1. Maximize blowdown, and add demineralized, deoxygenated makeup water. Check makeup purity.

Dissolved oxygen

1. Check hydrazine residual and add if required.
2. Check air inleakage.

Sodium/Chloride

1. Maximize blowdown, add demineralized, deoxygenated water.
2. Check makeup water purity.

## 2.4 Power Operation

### 2.4.1 Introduction

The parameters and operating ranges monitored during power operation are those currently considered appropriate to protect the steam generators and balance of plant. Utilities are encouraged to implement a more extensive surveillance program and to adopt lower levels of impurities whenever plant specific situations will allow.

Guidelines are provided for feedwater, blowdown and condensate sample sources (see Section 2.1.4). Action Level 2 control is placed on blowdown chloride, sodium and cation conductivity, and condensate oxygen. Action Level 3 control is placed on cation conductivity and sodium in the blowdown sample.

Guideline parameters are given in Table 2.3. Justifications are given in Section 2.4.3. Typical corrective actions are given in Section 2.4.4.



## 2.4.2 Tables of Parameters and Values

Table 2-3a

### RECIRCULATING STEAM GENERATOR POWER OPERATION FEEDWATER SAMPLE

<u>Parameter</u>	<u>Frequency</u>	<u>Normal Value</u>	<u>Action Level</u>		
			<u>1</u>	<u>2</u>	<u>3</u>
pH (ferrous system)	continuous	9.3-9.6	<9.3		>9.6
pH (ferrous/copper system)	continuous	8.8-9.2	<8.8		>9.2*
Cation Conductivity, $\mu$ mho/cm	continuous	<0.2		>0.2	
Sodium, ppb	continuous	<3		>3	
Dissolved O <sub>2</sub> , ppb	continuous	<3		>3	
Total Iron, ppb	weekly (integrated)	<20		>20	
Total Copper, ppb	weekly (integrated)	<2		>2	
Hydrazine, ppb	daily	>3 x [O <sub>2</sub> ]**		<3 x [O <sub>2</sub> ]**	
pH Control Additive	daily	***		***	

\* Action required only if experience shows increased copper transport at pH > 9.2

\*\* Based on oxygen value measured in the condensate sample

\*\*\* To be consistent with pH

Table 2.3b

RECIRCULATING STEAM GENERATOR  
POWER OPERATION  
BLOWDOWN SAMPLE

<u>Parameter</u>	<u>Frequency</u>	<u>Normal Value</u>	<u>Action Level</u>		
			<u>1</u>	<u>2</u>	<u>3</u>
pH (ferrous system)	continuous	>9.0	<9.0		
pH (ferrous/copper system)	continuous	8.5-9.2	<8.5 >9.2*		
Cation Conductivity, μmho/cm	continuous	<0.8	>0.8	>2	>7
Sodium, ppb	continuous	<20	>20	>100	>500
Chloride, ppb	daily	<20	>20	>100	
Silica, ppb	daily	<300	>300		

\* Action required only if experience shows increased copper transport at  
pH > 9.2

Table 2-3c

RECIRCULATING STEAM GENERATOR  
POWER OPERATION  
CONDENSATE SAMPLE

<u>Parameter</u>	<u>Frequency</u>	<u>Normal Value</u>	<u>Action Level</u>		
			<u>1</u>	<u>2</u>	<u>3</u>
Dissolved O <sub>2</sub> , ppb (ferrous system)	continuous	<10	>10	>50	
(ferrous/copper system)	continuous	<10	>10	>30	

### 2.4.3 Justification for Parameters and Values

pH: The feedwater pH range depends upon the materials in the feedtrain. Ammonia is the volatile amine normally used for feedwater pH control; however, other amines, such as morpholine or cyclohexylamine, may be used with the adjustment of other guideline parameters. Thermal decomposition of hydrazine to ammonia will affect pH.

Plants with all ferrous feedtrains operate with a feedwater pH in the range of 9.2-9.6 [5]. Plants with copper alloys in the feedtrain normally operate in the range 8.8-9.2 [6]. Operation within these ranges will maintain the long-term integrity of the feedtrain and minimize the amount of corrosion product transport to the steam generators. Below a pH of 8.8 ferrous corrosion increases, while at pH >9.2 copper alloy corrosion may increase. Operation at pH > 9.2 is permissible if experience shows that copper transport is not increased.

The pH of the steam generator blowdown is controlled by the concentration of ammonia and hydrazine present in the feedwater in the absence of significant impurity ingress, alternative chemistries or primary to secondary leakage. All-volatile treatment has no buffering capacity against strongly ionized impurities; consequently, the comparison of pH measured and pH calculated from ammonia concentration (Figure 2-3) could be employed to identify any increases in the concentration of acidic or alkaline species in the steam generator bulk water.

Cation Conductivity: Cation conductivity is used to detect the ingress of soluble anionic impurities. Feedwater cation conductivity values less than 0.2  $\mu\text{mho/cm}$  are needed to meet the blowdown cation conductivity values. This parameter is a measure of the total concentration of anions which are present in the steam generator bulk water.

Blowdown cation conductivity values of  $\leq 0.8 \mu\text{mho/cm}$  represent acceptable operating practice based on plant experience. Small condenser leaks or other forms of contaminant ingress result in Action Level 1 values prior to steam generator corrosion. Action Level 2 comes into effect at 2-7  $\mu\text{mho/cm}$ , a level

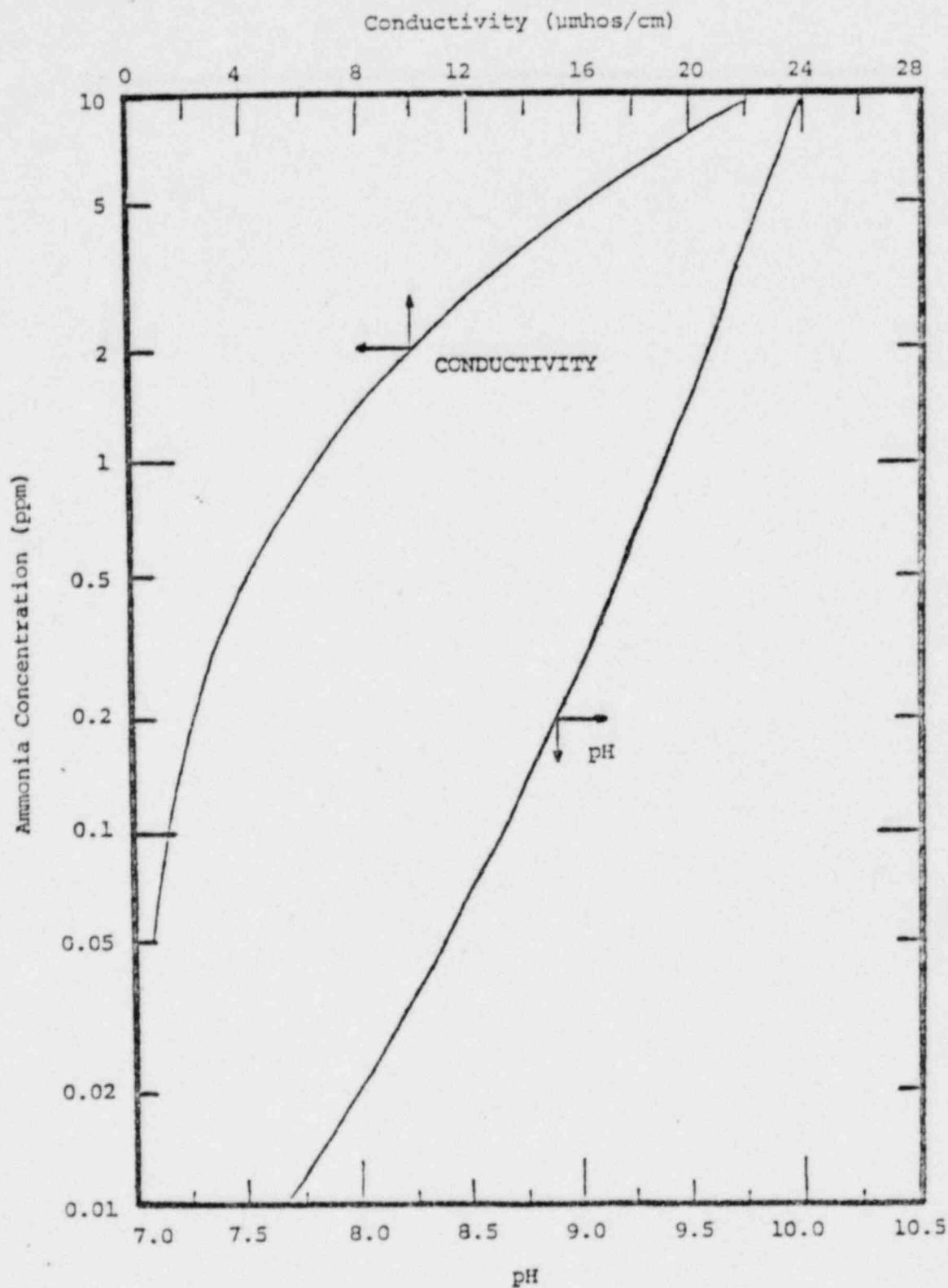


Figure 2-3. VARIATION OF SOLUTION pH AND ELECTRICAL CONDUCTIVITY WITH AMMONIA CONCENTRATION AT 25°C IN THE ABSENCE OF OTHER IONIC SPECIES

at which denting has occurred in plants operating at full power. Power reduction to <30% will significantly reduce heat flux in areas of the steam generator where denting normally occurs while maintaining sufficient system flow for automatic control while the leak is located and repaired. To minimize steam generator corrosion, Action Level 3 is instituted if 7  $\mu\text{mho/cm}$  is exceeded. If a condenser leak cannot be confirmed following an increase in cation conductivity, analysis for specific anions not normally measured (such as sulfates) should be considered.

Sodium: The values represent operating practice based on plant experience. Exceeding the blowdown levels of Action Level 2 increases the possibility of caustic stress corrosion cracking (SCC) of Inconel 600. This is based on service experience and laboratory tests at higher concentrations. Sodium is an effective continuous indicator of many forms of contaminant ingress and should be used as such.

Chloride: Chloride is aggressive to ferrous materials at steam generator conditions [7]. Anions of other strong acids such as sulfate, etc., may also be aggressive, however, their aggressiveness is governed by their relative strengths as corrodents, their ability to diffuse to the corrosion interface and their concentration in the crevice region. Currently, chloride has proved to be the most common aggressive anion found in the crevice region.

Sample tube/support plate crevices removed from dented steam generators have shown local chloride concentrations of over 4,000 ppm. A contributing cause to this high local chloride concentration is the local thermal-hydraulic condition in the tube/support plate crevice.

Chlorides can form acid chlorides in the crevice which are believed to be a major factor in the growth of nonprotective magnetite [8,9]. The presence of a reducible species can promote the formation of acidic crevice conditions. Some common reducible species are oxygen, Cu(II), Ni(II), or Fe(III).

Silica: To control silica volatility and subsequent precipitation on the turbine, as well as formation of silicate deposits in the steam generator, a blowdown value of <300 ppb has been established. This level is based upon operating experience.

Dissolved Oxygen: Corrosion product formation and transport is minimized by control of oxygen and pH. The removal of low levels of dissolved oxygen is achieved by addition of excess hydrazine.

Dissolved oxygen is monitored in the feedwater and in the condensate (Section 2.1.4 describes sample sources). Action Level 2 is instituted when dissolved oxygen in the condensate exceeds guideline recommendations.

Dissolved oxygen, in the absence of other aggravating species, forms magnetite ( $\text{Fe}_3\text{O}_4$ ) on carbon steel surfaces at temperatures above approximately 100°C. If the magnetite film formed is impervious and self-repairing the film is termed protective magnetite. Nonprotective magnetite is formed when solution chloride is combined with nickel, cobalt, vanadium or antimony [7]. Linear (nonprotective) magnetite growth can lead to eventual tube constriction known as "denting." Recent laboratory studies have shown that copper (II) chloride or oxide can be an accelerant [10], and that nonprotective magnetite can form with neutral chlorides in the presence of oxygen [11]. Copper oxides are transported through the reaction of oxygen with copper feedtrain materials.

The evidence for the damaging effects of dissolved oxygen, and of oxide reaction products is abundant. Every effort should be made to control air ingress and dissolved oxygen levels.

Iron: Total iron is monitored to quantify the transport and buildup of sludge in the steam generators and to monitor feedtrain corrosion. The feedwater specification of <20 ppb is based on extensive plant data [12,13,14,15].

Copper: Total copper is monitored to quantify the transport and buildup of sludge in the steam generators and to monitor feedtrain corrosion. The feedwater specification of <2 ppb is based on extensive plant data [12,13,14,15]. Laboratory model boiler denting tests indicate that higher concentrations of reducible copper species in the feedwater increases the denting rate [10].



Hydrazine: Oxygen will react with hydrazine to form water, hydrogen and nitrogen, depending upon the reaction conditions [16]. Under feedtrain conditions it is assumed that oxygen/hydrazine reactions occur at the metal oxide or hydroxide surface. Reaction rates increase with pH, hydrazine excess, and temperature and may depend on the surfaces contacted. Control of air inleakage and the use of hydrazine as a scavenger of trace quantities of dissolved oxygen reduces the corrosion of balance of plant materials. This yields a reduction in the transport of corrosion products to the steam generators.

Hydrazine decomposes to ammonia under steam generator operating conditions [17] and will travel with the steam to the condenser where the bulk of the ammonia dissolves in the condensate. This will aid in pH control; however, excessive ammonia levels must be avoided in copper alloy systems.

pH Control Additive: Analysis for pH control additive in the feedwater is performed to cross-check on pH measurements.

Analysis of ammonia is required primarily for protection of copper alloys. Additionally, a direct comparison can be made between measured pH with measured ammonia (Figure 2-3). Deviation from the predicted curve provides an early indication of impurities such as  $\text{CO}_2$  or other anions which can cause suppression or elevation of the pH. These impurities should be verified by other analyses.

#### 2.4.4 Corrective Action Guidelines - Power Operation

##### Steam Generator Feedwater

<u>Parameter Out of Range</u>	<u>Corrective Action</u>
pH	<ol style="list-style-type: none"><li>1. Check ammonia and/or hydrazine feed rate and adjust if necessary.</li><li>2. Increase blowdown, if required.</li><li>3. Test outlet of each condensate polisher tank and each makeup demineralizer tank.</li></ol>
Cation conductivity and sodium	<ol style="list-style-type: none"><li>1. Increase steam generator blowdown.</li><li>2. Institute sampling of condenser sections.</li><li>3. Sample all makeup sources.</li><li>4. Test effluents of makeup demineralizers and polishing demineralizers.</li></ol>
Dissolved oxygen	<ol style="list-style-type: none"><li>1. Check residual hydrazine; if below normal, increase feed rate.</li><li>2. Check condenser air leakage rate.</li><li>3. Test other available locations in feedwater train for dissolved oxygen.</li></ol>
Iron and Copper	<ol style="list-style-type: none"><li>1. Check dissolved oxygen, condenser air inleakage, pH and ammonia.</li></ol>
Hydrazine	<ol style="list-style-type: none"><li>1. Increase feed rate. Check ammonia and feedwater pH.</li></ol>

##### Steam Generator Blowdown

<u>Parameter Out of Range</u>	<u>Corrective Action</u>
pH	<ol style="list-style-type: none"><li>1. Check feed rate of hydrazine and ammonia.</li><li>2. Test effluent of demineralizers for presence of caustic or acid.</li><li>3. Increase blowdown if appropriate.</li></ol>
Cation conductivity, sodium, chloride and silica	<ol style="list-style-type: none"><li>1. Increase blowdown.</li><li>2. Institute sampling of condenser sections.</li><li>3. Test effluent of demineralizer tanks.</li></ol>

##### Condensate

<u>Parameter Out of Range</u>	<u>Corrective Action</u>
Dissolved O <sub>2</sub>	<ol style="list-style-type: none"><li>1. Check condenser air leakage rate.</li><li>2. Test other available locations in feedwater train for dissolved oxygen.</li></ol>

## 2.5 References

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