

# KANUPP – IAEA Training

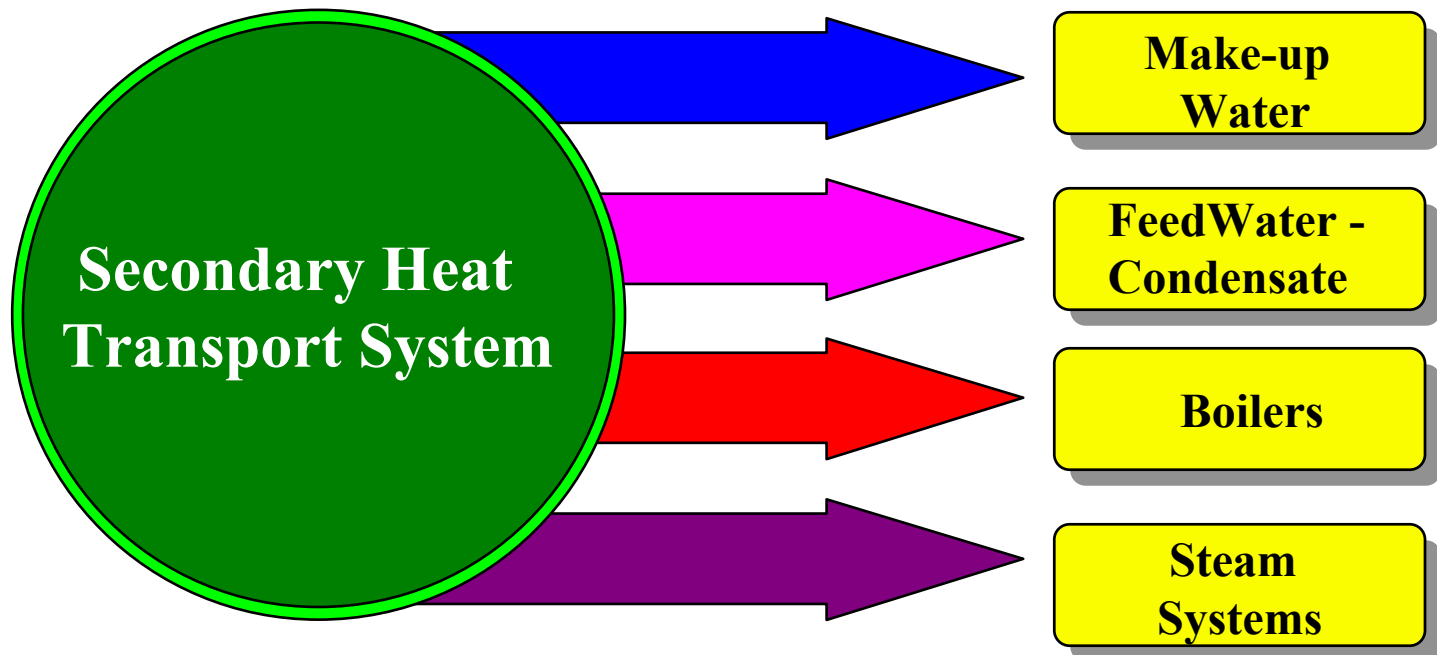
Steam Generator  
Chemistry Control

# **Steam Generator Water Chemistry**

## **Course Objectives**

- **State the consequences of out of spec parameters on Secondary Side plant systems and components.**
- **Recognize condenser sea water leak indications; state the concerns and general procedure to follow in the event of a condenser sea water leak**
- **State what indications are in place to give indication of a Steam Generator Tube leak.**
- **State the main concerns associated with a Steam Generator Tube leak.**

# CONDENSATE FEEDWATER - BOILER SYSTEM



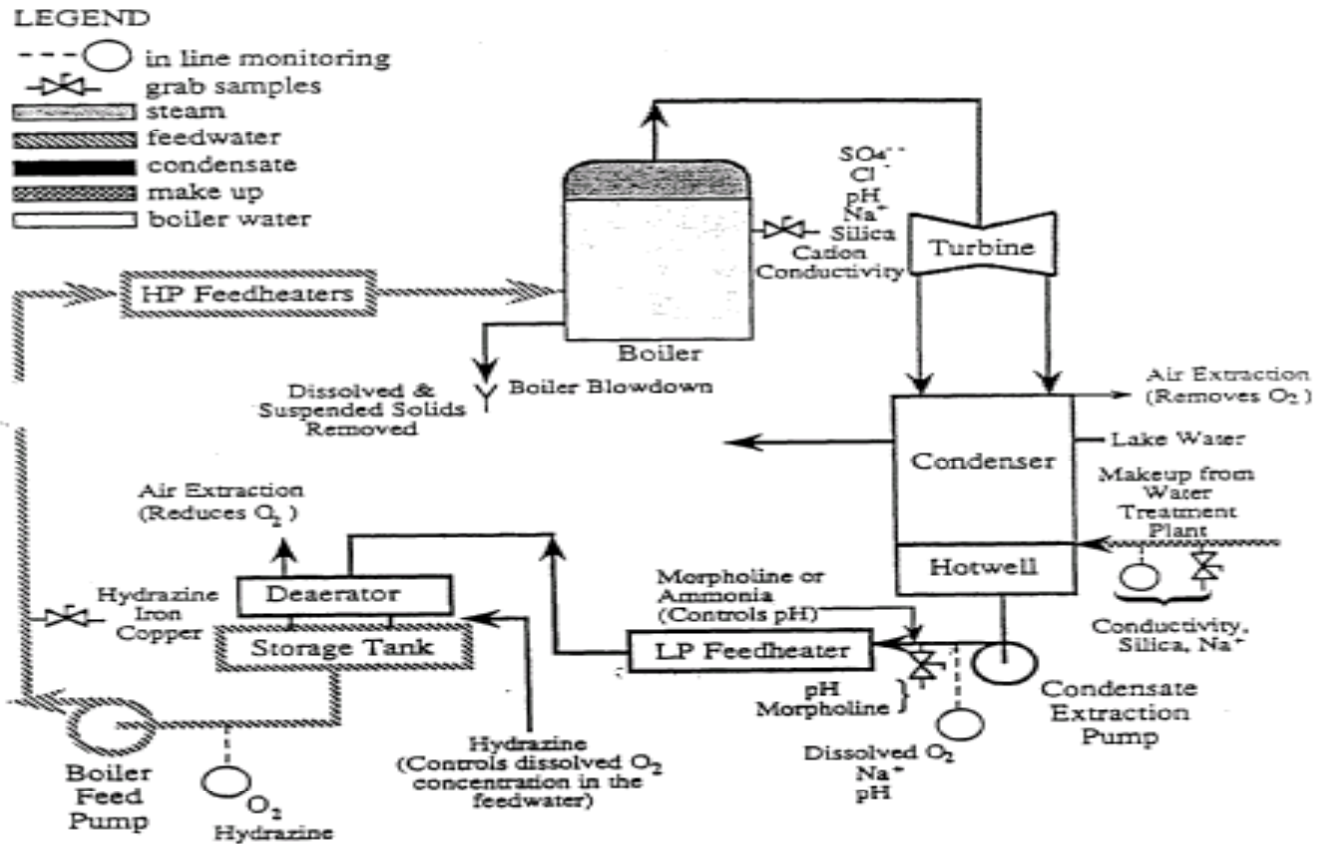
## **Chemistry Objectives**

- **Minimize Corrosion in order to preserve system integrity and ensure the long term availability of equipment.**
- **Minimize Local Corrosion of Boiler materials which can occur in regions of restricted flow, particularly under deposits and within crevices.**
- **Minimize transport of corrosion products into the Boilers (condensate - feedwater corrosion).**
- **Minimize erosion in steam - turbine - feedwater - condensate.**

## **Steam System Chemistry Control**

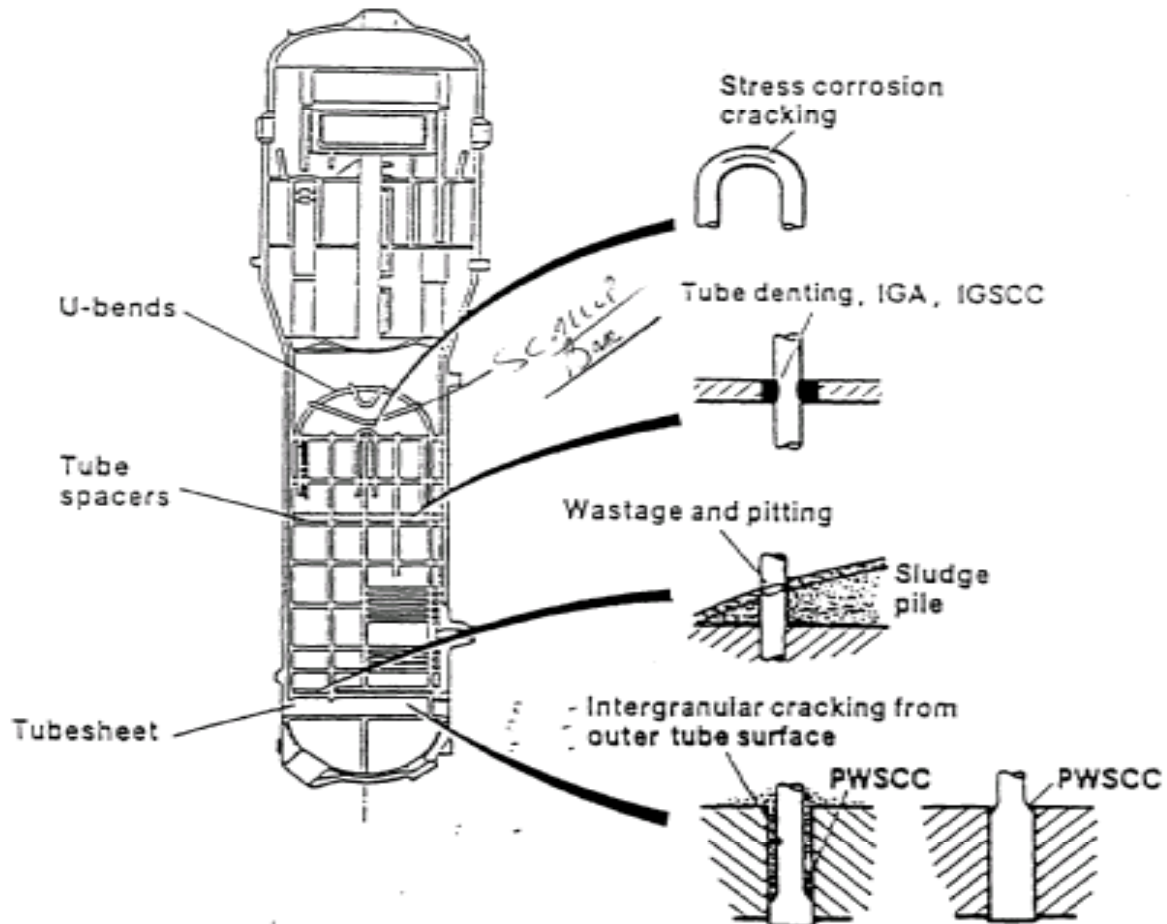
- **Maintaining alkaline pH conditions in the water systems:**  
Accomplished with the addition of morpholine.
- **Reduction in Erosion/Corrosion in Two-Phase wet steam regions is particularly important.** The key is to maintain pH in the liquid phase high enough to minimize carbon steel corrosion. This is more easily achieved with Morpholine, which tends to remain in the liquid phase due to its more favourable distribution ratio, as compared to ammonia which favors the steam phase.

## Condensate - Feedwater - Boiler System Chemistry Control



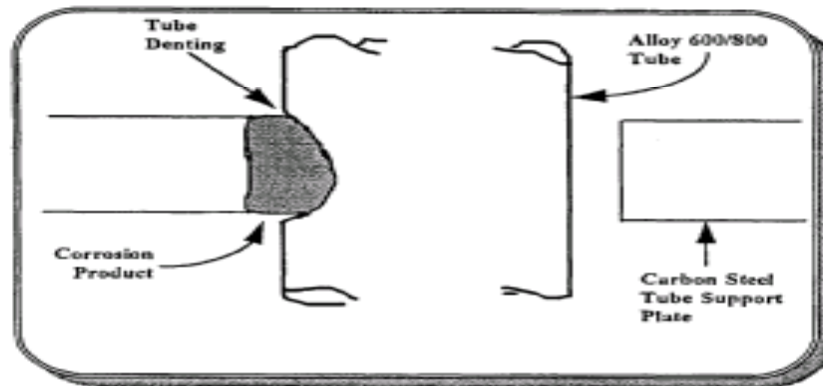
Overhead 52  
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# TYPICAL CORROSIVE ATTACKS IN STEAM GENERATORS



Overhead 40  
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# STEAM GENERATOR TUBE DENTING



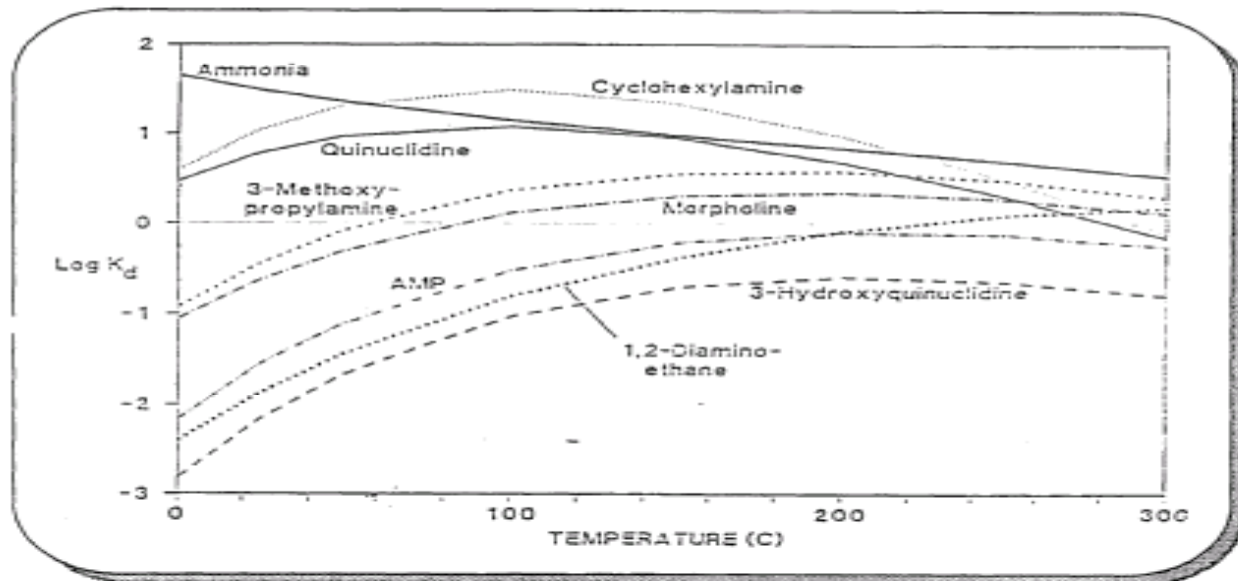
- **Denting is a form of “Crevice Corrosion”.** Denting is the inward displacement or Dent of the SG tubing at the tube/tube support plate intersections.
- **Denting is caused by the approximately two-fold increase in volume of oxides that form when accelerated corrosion of the carbon steel occurs in the drilled holes of the tube support plates.**
- **Chloride solutions are the major contributor to SG tube denting.**

Overhead 42

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# Distribution Ratios of Various Amines

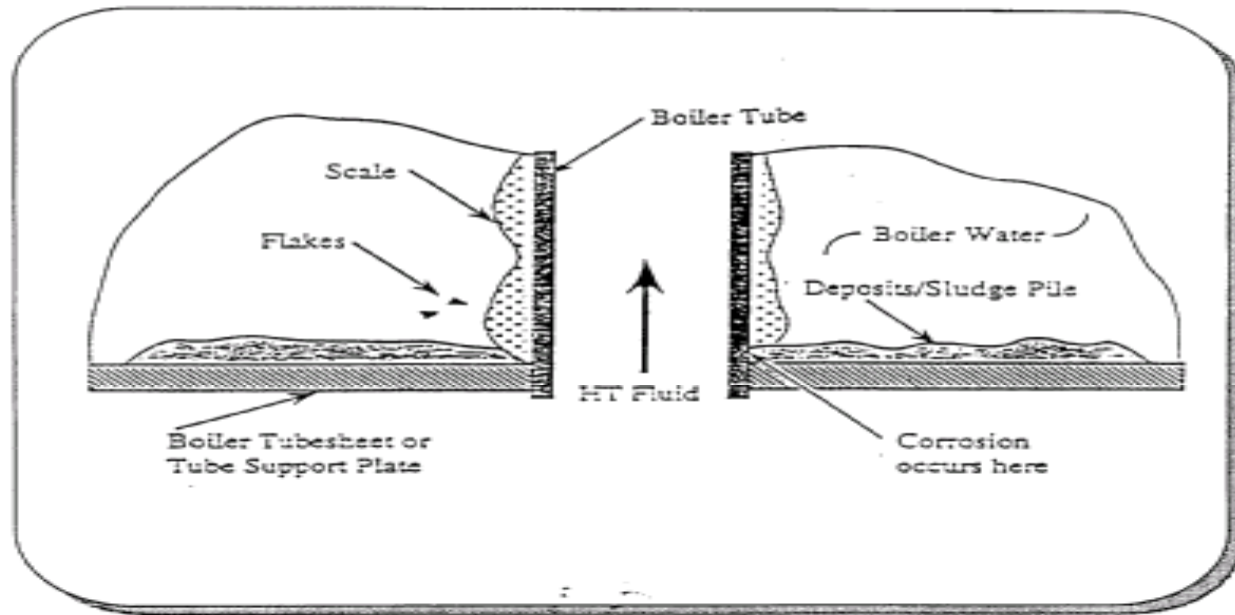


$$K_d = \frac{\text{Concentration of amine in the steam phase}}{\text{Concentration of amine in the liquid phase}}$$

Overhead 47

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# BOILER TUBE SCALE AND TUBESHEET DEPOSITS



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# **ADVERSE EFFECTS OF SLUDGE AND SCALE**

- **Soluble impurities concentrate in sludge by factors of 10,000 to 100,000, creating a very hostile environment with respect to corrosion.**
- **Under Deposit Corrosion of tubes beneath the sludge pile via pitting and/or caustic attack.**
- **Sludge, over time becomes extremely difficult to remove (like concrete).**
- **Reduced Heat Transfer through boiler tube walls, unit efficiency drops.**
- **Possible shorter tube life resulting in heat transfer leak into the boiler, if through wall corrosion occurs.**
- **Production concerns.**
- **Deposits on tube support may lead to level control problems.**

Overhead 50

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## SLUDGE AND SCALE FORMING SUBSTANCES

TYPE		SOURCES
Suspended Inorganic Solids (Particulates)		Corrosion in boiler steam and feed water system. Ingress of raw water via condenser tube leaks.
Dissolved Inorganics Materials	Ca & Mg Bicarbonates	Raw water via condenser tube leaks.
	Silica	Traces in makeup. WTP IX breakthrough. Condenser tube leaks.
	Na <sup>+</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> Ions	Traces in makeup. Condenser tube leaks. Na <sup>+</sup> from WTP IX breakthrough.
	Corrosion Products	Feed train corrosion.

# MAJOR BOILER STEAM AND WATER SYSTEM MATERIALS

COMPONENT	PNGS - A	PNGS - B	BNGS - A	BNGS - B	DNGS	PLGS
STEAM GENERATOR TUBES	Monel - 400	Monel - 400	Inconel - 600	Inconel - 600	Incoloy - 800	Incoloy - 800
H.P. HEATER TUBES	90/10 Cu/Ni	90/10 Cu/Ni	90/10 Cu/Ni	Stainless Steel	Stainless Steel	Stainless Steel
H.P. HEATER SHELL	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel
L.P. HEATER TUBES	Admiralty Brass	Admiralty Brass	Admiralty Brass	Stainless Steel	Stainless Steel	Stainless Steel
L.P. HEATER SHELL	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel
FEEDWATER PIPING	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel
CONDENSER TUBES	Admiralty Brass	Admiralty Brass	Admiralty Brass	Stainless Steel	Stainless Steel	Titanium
CONDENSER SHELL	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel
DAERATOR	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel
TURBINE BLADES	Stainless Steel	Stainless Steel	Stainless Steel	Stainless Steel	Stainless Steel	Stainless Steel

Incoloy 800

Stainless Steel

Carbon Steel

SS

CS

CS

Titanium

CS

SS

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# KANUPP Boiler/Boiler Feedwater System Chemistry Specification

		<u>Specified *</u>	<u>Recommended</u>
• pH	=	8.8 to 9.5	> 9
• Hydrazine	=	< 50 ppb	to provide O<10
• Morpholine	=	10 to 16 ppm	to provide pH>9
• Dissolved Oxygen	=	< 10 ppb	< 10 ppb
• Iron	=	Not defined	< 10 ppb
• Copper	=	< 0.5 ppm	< 10 ppb
• Nickel	=	Not defined	ND
• Aluminum	=	Not defined	ND
• Zinc	=	Not defined	ND
• Silica	=	< 10 ppm	< 0.5 ppm
• Chloride	=	< 1 ppm	< 50 ppb
• Hardness	=	< 1 ppm	ND

Note: \* Wilayat Hussain Aug 1981

# KANUPP Boiler System

## Features Important to Chemistry Control

- |                                      |     |       |                 |
|--------------------------------------|-----|-------|-----------------|
| Boiler steam flow rate Mg/hr (lb/hr) |     | 0.748 | (1.65 E6 lb/hr) |
| Moisture in steam                    | - % | < 1 % |                 |
  
- |                                 |    |    |               |
|---------------------------------|----|----|---------------|
| Boiler water volume (6 boilers) | Mg | 60 | (13,200 Igal) |
|---------------------------------|----|----|---------------|
  
- |                    |          |      |                 |
|--------------------|----------|------|-----------------|
| Full blowdown rate | - Kg/min | 283  | (62.5 Igal/min) |
|                    | - % MSR  | 2.3% |                 |
  
- |                               |            |
|-------------------------------|------------|
| Cleanup half-time by blowdown | 2.44 hours |
|-------------------------------|------------|

# Phosphate Chemistry Control

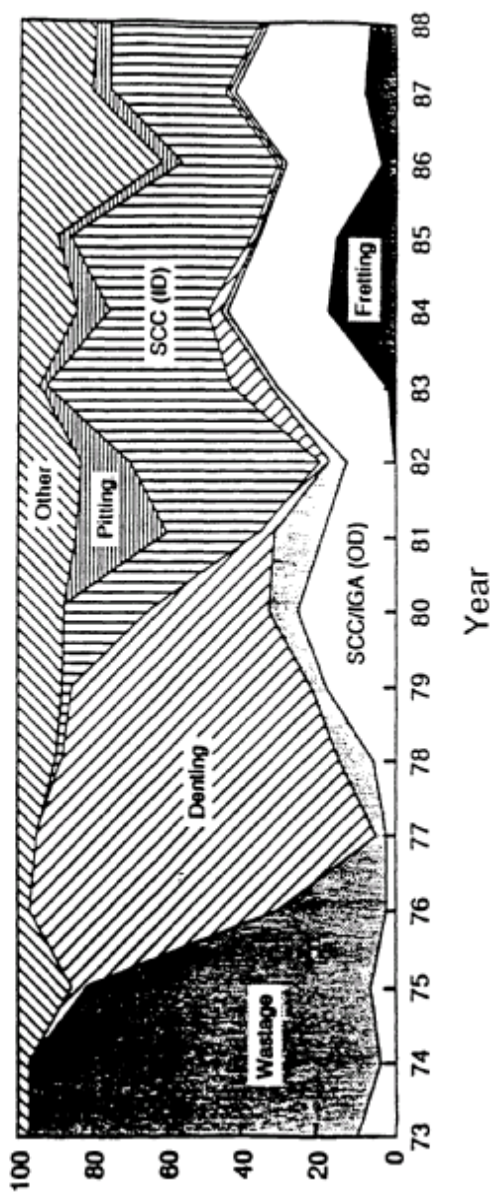
- **Salts can enter the Boilers from the Water Treatment Plant, Leakage of Condenser Tubes or from the Condensate Polisher Resins. These salts can concentrate within crevices or under deposits producing Acidic or Caustic conditions leading to localized corrosion of Boiler Tubes or components.**
- **Phosphate Salts (a mixture of mono & trisodium phosphate) are added to the water to provide “Buffering Capacity” to the water. In other words to prevent acidic or caustic conditions from occurring.**
- **The phosphate salts also convert scale-forming impurities, such as calcium and magnesium, to precipitates which may then be removed by blowdown.**



# Phosphate Chemistry Control

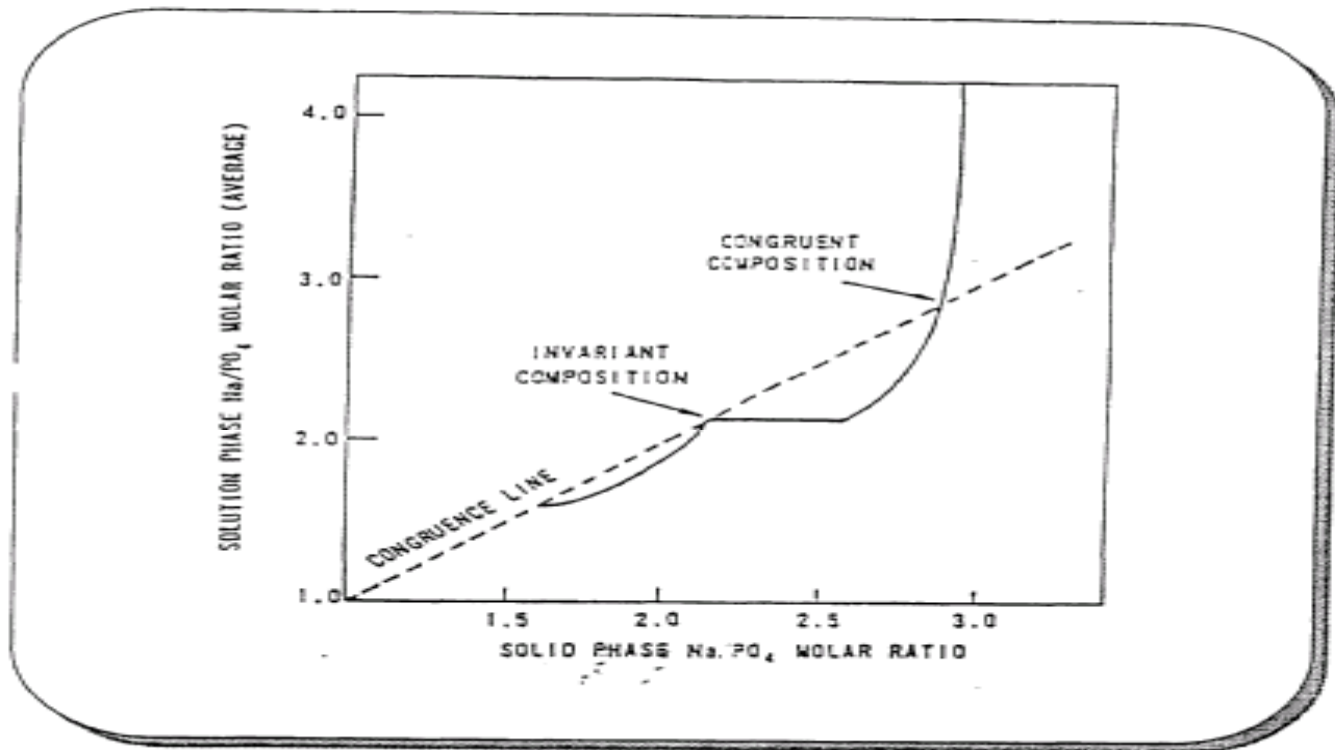
- **Phosphate Chemistry Control is based on the addition of a mixture of Mono and Trisodium Phosphate to the water.**
- **Control is based on a term called Z-Phos. This is defined as the ratio of moles of sodium ions and hydroxyl ions to the total moles of phosphate ions in solution.**
- **Z-Phos is controlled in the range of 2.2 to 2.6 for water treatment. Z-phos values of 3 or greater will result in excess NaOH in the sludge. Z-Phos values less than 2 can lead to acidic conditions in the sludge.**
- **Z-Phos is controlled by varying the concentrations of mono and trisodium phosphate feed to the Boilers.**
- **Phosphate concentrations in the Boilers is controlled under normal conditions in the range of 3 to 5 mg/Kg.**

# WORLD WIDE CAUSES OF STEAM GENERATOR PLUGGING Tube Failure Mechanisms



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# Congruent Phosphate Treatment



Relationship between Na/PO<sub>4</sub> Ratios of Solid and Solution Phases

Overhead 55

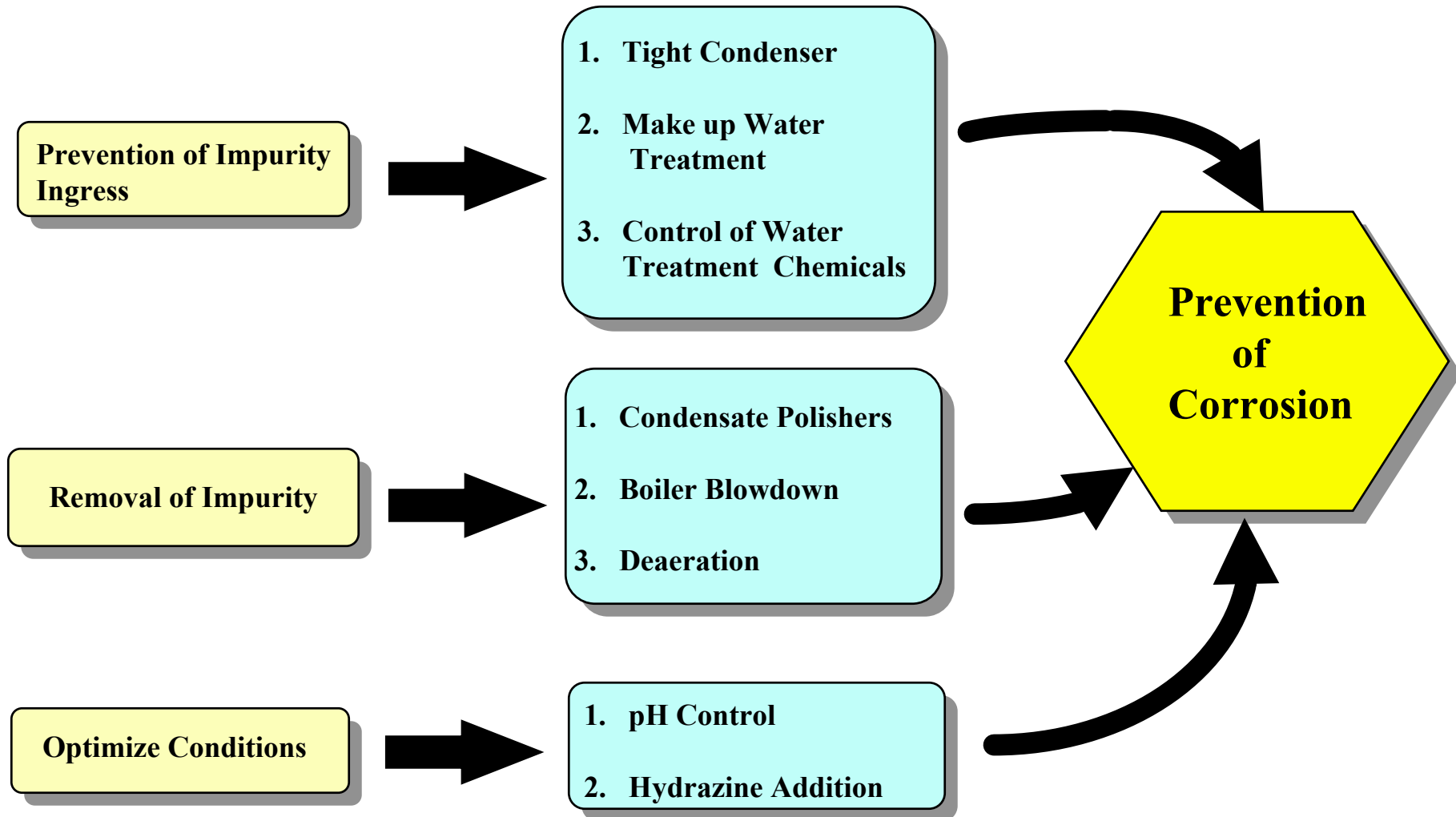
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## Phosphate Chemistry Control versus All Volatile Treatment

<u>Parameter Monitored</u>	<u>AVT Chemistry Spec</u>	<u>Phosphate Chemistry Spec</u>
Cation Conductivity	0.3 mS/m	not monitored
pH	8.7 - 9.7	8.7 - 9.7
Chloride	< 20 ppb	< 2 ppm
Sodium	< 20 ppb	2 - 5 ppm Based on Z-Phos

Overhead 59A  
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# BASIC PHILOSOPHY OF SECONDARY WATER CHEMISTRY CONTROL



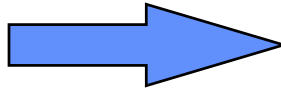
# **Steam Generator Tube Failures**

- **During normal operation a very small quantity of tritium permeates through the steam generator tubing (diffusion). The permeation occurs with the hydrogen and deuterium escaping from the PHT system.**
- **Due to this diffusion, a small quantity of tritium will be present in the steam generator water and steam ..... current tritium concentrations in the steam generator steam samples is about  $3.0 \times 10^4$  Bq/Kg.**
  - during normal operation when there is no D<sub>2</sub>O leakage, no noble gases or fission products will be found in the secondary side water (S/G, feedwater or steam).
- **This changes when there is a leakage of PHT water through the steam generator tubing. When a leakage occurs, the secondary side will have some noble gases, fission products and increased tritium concentrations.**

# Steam Generator Tube Failures

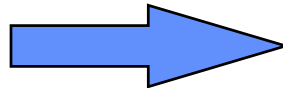
## Distribution of radionuclides in the secondary side water

**Noble Gases**



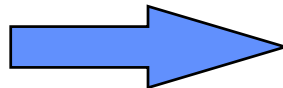
- Carries over with the steam.
- Removed in the condenser air extraction zones.

**Radioiodines**



- Remains in the Boiler water.
- Removed via blowdown

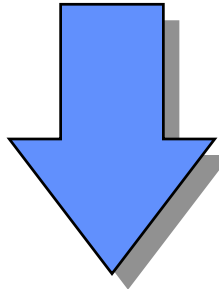
**Tritium**



- Mixes equally with the steam and water.
- Escapes with both the water and steam.

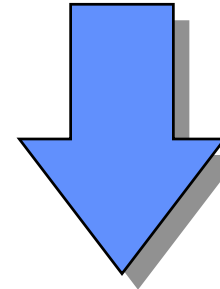
# Steam Generator Tube Failures

## Impact of S/G Tube Leaks



### Environmental

- Less significant than Economic
- Radioiodine most significant emission.
- Minimized by maintaining max. PHT purification flow.  
*Prompt removal of defective fuel*



### Economic

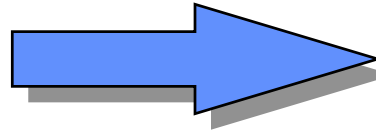
- 1 Kg D<sub>2</sub>O/hr --- @ \$300/hr
- 5 Kg D<sub>2</sub>O/hr --- @ \$1500/hr
- 10 Kg D<sub>2</sub>O/hr --- @ \$3000/hr



# Steam Generator Tube Failures

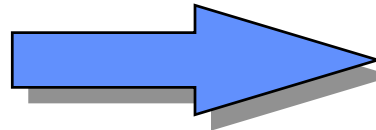
## Steam Generator Tube - Leak Detection

**Barringer D<sub>2</sub>O in H<sub>2</sub>O  
Leak Detection System**



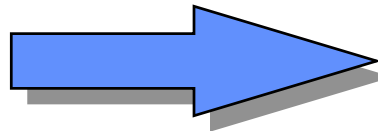
- Two Infrared Detectors.  
*(one for boiler streams the other for RCW)*
- BO1 steam monitored continuously.  
*(BO1 to BO4 B/D can be manually valved in)*
- Alarms at 160 mg/Kg D<sub>2</sub>O in H<sub>2</sub>O  
*(normal background approx. 140 mg/Kg)*

**Radioactivity in Boiler Water**



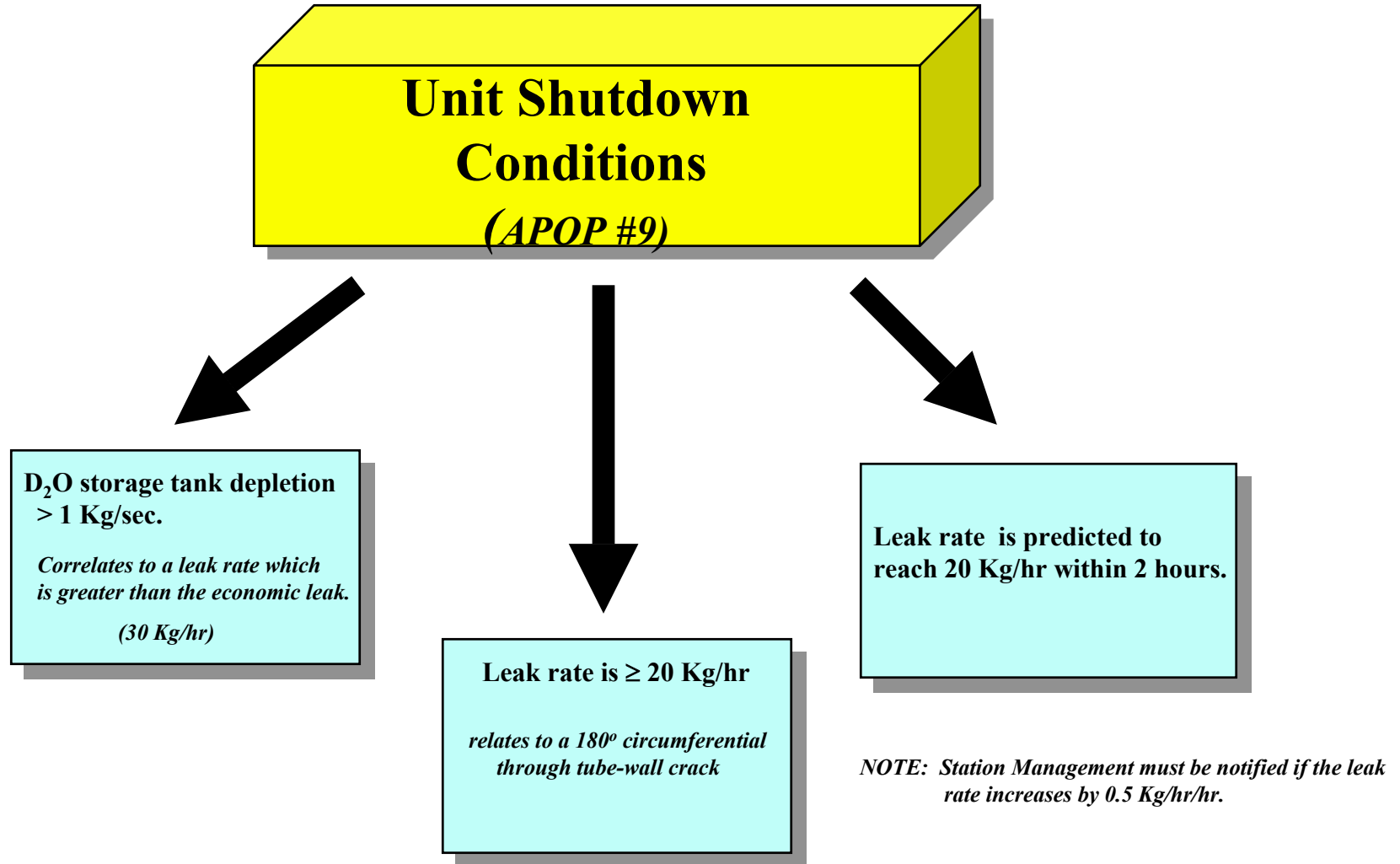
- Measures gross gamma activity in the boiler blowdown water.  
*(composite of all 4 boilers)*
- Alarms at 250 cps.

**Manual Sampling**



- Individual boiler steams sampled 1/day.
- Normal steam tritiums (no tube leaks) is about  $3.0 \times 10^4$  Bq/Kg.
- $2.0 \times 10^7$  Bq/Kg corresponds to a leak rate of about 2.0 Kg/hr.

# Steam Generator Tube Failures



# Sampling Requirements during a Steam Generator Tube Leak

S a m p l e P o i n t	F r e q u e n c y	A n a l y s i s
B o i l e r # 1 S t e a m	2 / S h i f t	T r i t i u m
B o i l e r # 2 S t e a m	2 / S h i f t	T r i t i u m
B o i l e r # 2 S t e a m	2 / S h i f t	T r i t i u m
B o i l e r # 2 S t e a m	2 / S h i f t	T r i t i u m
B o i l e r B l o w d o w n C o m p o s i t e	1 / S h i f t	G a m m a S c a n
C E P	2 / S h i f t	T r i t i u m / I s o t o p i c
D e m i n W a t e r M a k e - u p t o t h e R F T T o t a l i z e r R e a d i n g	2 / S h i f t	
L a g o o n # 1 & # 2	2 / S h i f t	T r i t i u m / I s o t o p i c
I n S e r v i c e L a g o o n S l u d g e	2 / S h i f t	G a m m a S c a n