Saline Water Conversion Corporation
www.swcc.com

CARBOHYDRAZIDE vs HYDRAZINE: A Comparative Study

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BACKGROUND

- Saline Water Conversion Corporation (SWCC) produces electricity and drinking water through its dual-purpose plants. The total power generated from all these plants exceeds 5000 MW. This enormous power is being generated from 55 high pressure boilers.

- Hydrazine has been extensively used in SWCC high pressure boilers as an effective oxygen scavenger for the last several decades. However, recent studies with hydrazine have indicated some difficulties both of technological nature and those connected with its toxicity and explosion hazards.

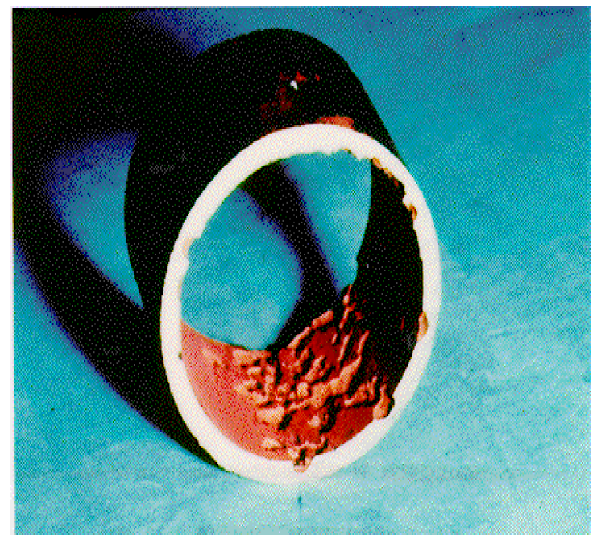
- Despite the fact that all SWCC power plants are taking necessary safety measures while handling hydrazine, it has become a serious desire of the top SWCC management to search for a suitable alternative to hydrazine for all SWCC boilers, that provides excellent oxygen scavenging, non-toxic and safe while handling.

PURPOSE OF OXYGEN CORROSION CONTROL

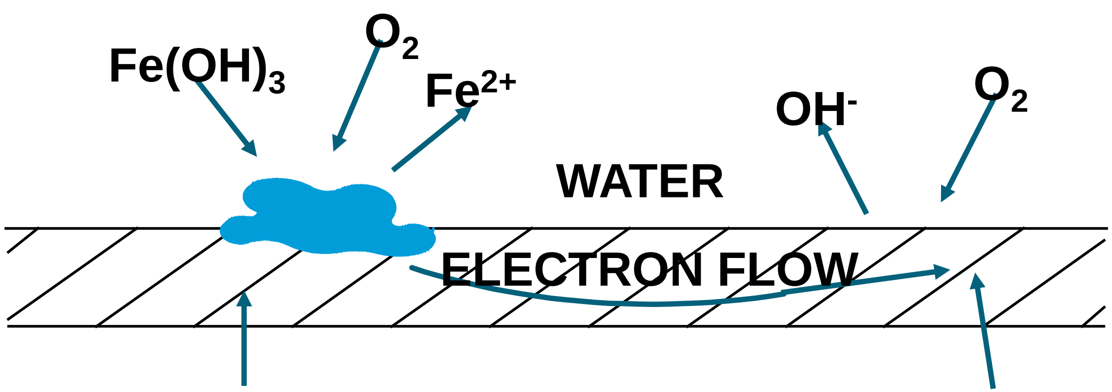
- **FAILURE PREVENTION**
  - Corrosion Minimisation
- **EQUIPMENT RELIABILITY**
  - Uninterrupted Production
  - Routine Maintenance
    - reduces crisis maintenance
    - allows planned preventive maintenance
- **ECONOMICS**
  - Decrease Overall Maintenance Cost
  - Decrease Downtime Cost

OXYGEN CORROSION

- CORROSION RATE DOUBLES WITH EVERY 10°C INCREASE IN WATER TEMPERATURE
- METAL LOSS
- LOCALISED
- RAPID FAILURE
- PIT FORMATION



DETAILED OXYGEN CORROSION OF IRON



ANODE

<u>ANODE REACTION</u>

$Fe_{\cdot} = Fe^{++}\ 2e^-$

CATHODE

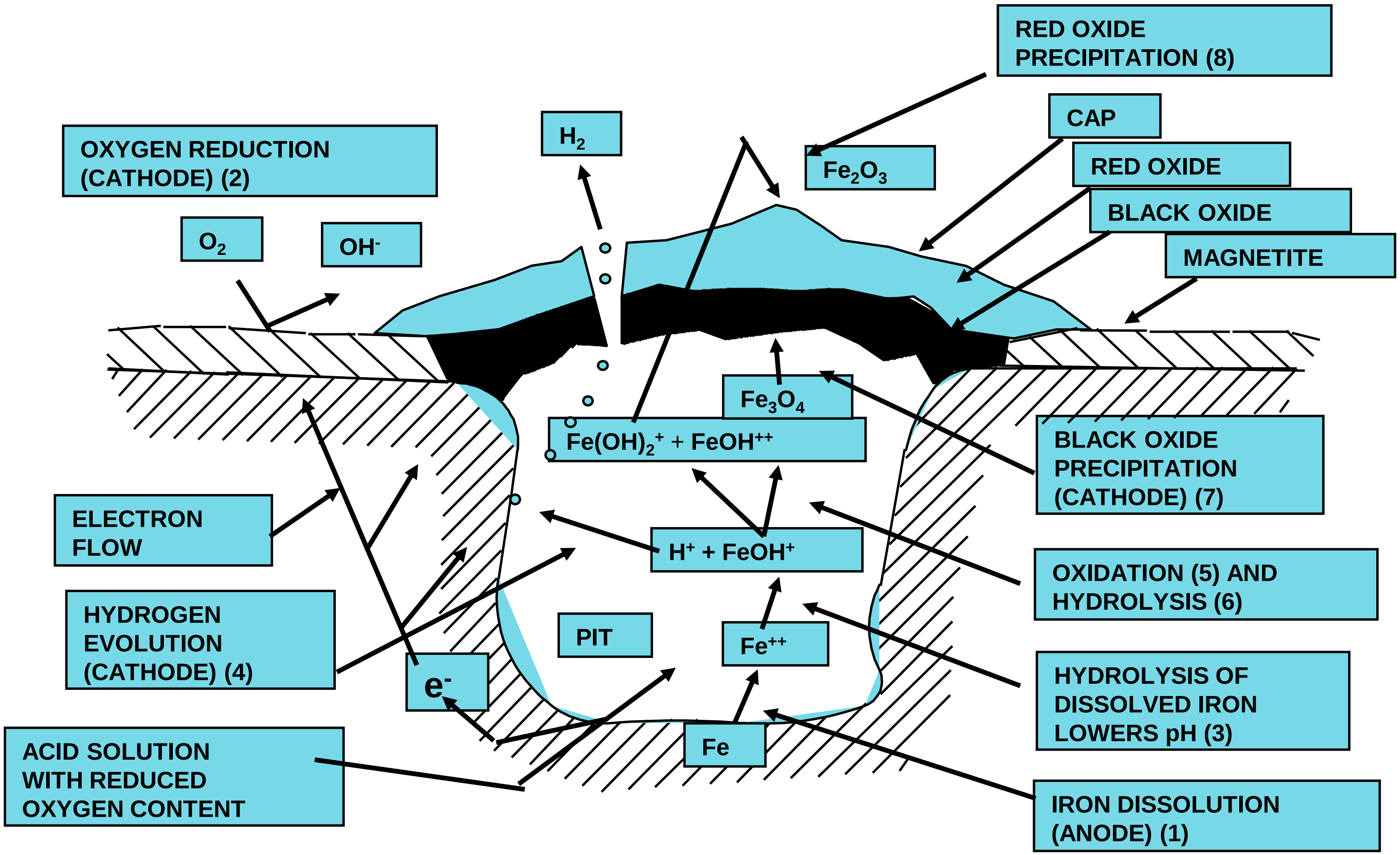
<u>CATHODE REACTION</u>

$1/2\ O_2 + H_2O + 2e^- = 20H^-$

MECHANISM

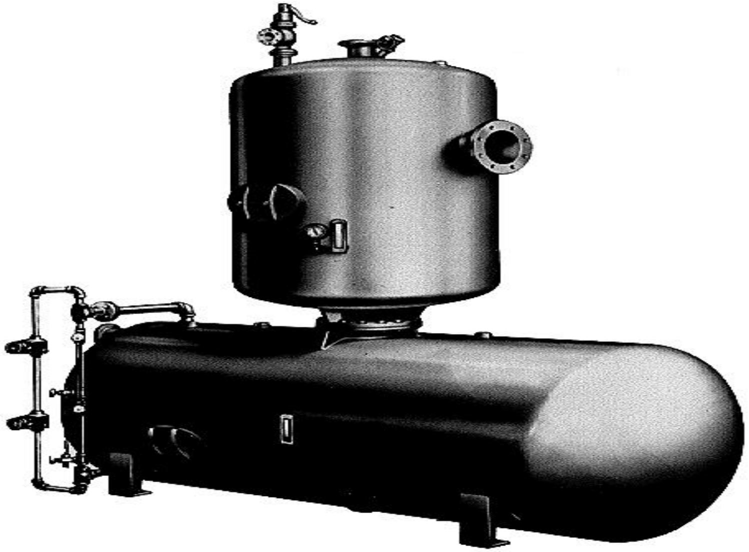
- IRON IS OXIDISED ON THE SURFACE (ANODE) - METAL LOSS
- OXYGEN IS REDUCED (CATHODE)

DETAILED OXYGEN CORROSION OF IRON



OXYGEN CONTROL PROGRAM

- **MECHANICAL**
  - Deaerators



- **CHEMICALS**
  (Oxygen Scavengers)

TYPES OF OXYGEN SCAVENGERS

- **INORGANIC** (non volatile)
  - **Contribute to the TDS of the Boiler Water**
- **ORGANIC** (volatile)
  - **Do NOT contribute to the TDS of the Boiler Water**

- **SOLID**
  - **SODIUM BISULFITE**
  - **SODIUM SULFITE**
- **NON-SOLIDS**
  - **HYDRAZINE**
  - **HYDROQUINONE**
  - **DEHA**
  - **CARBOHYDRAZIDE**
  - **ASCORBIC ACID**
  - **ISO-ASCORBIC ACID**

Sulphite

❖ REACTION:

- $2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$

❖ SCAVENGER DECOMPOSITION:

- $Na_2SO_3 + H_2O \longrightarrow SO_2 + 2\,NaOH$
- $4\,Na_2SO_3 \longrightarrow 3\,Na_2SO_4 + Na_2S$
- $Na_2S + 2H_2O \longrightarrow NaOH + H_2S$

Sulphite

ADVANTAGES:

- TRUE RESIDUAL TEST
- VERY FAST REACTIVITY WITH OXYGEN
- AVAILABLE IN LIQUID AND DRY FORMS
- INEXPENSIVE
- SULFITE : FDA Approved

DISADVANTAGES:

- CONTRIBUTES TO TDS
- BREAKS DOWN AT 42 Kg/cm^2 DRUM PRESSURE

Hydrazine

- **REACTION:**

  $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$

- **DECOMPOSITION REACTION:**

  $2N_2H_4 + \text{HEAT} + 2H_2O \longrightarrow 4NH_3 + O_2$

- **CONTROL LIMITS:**

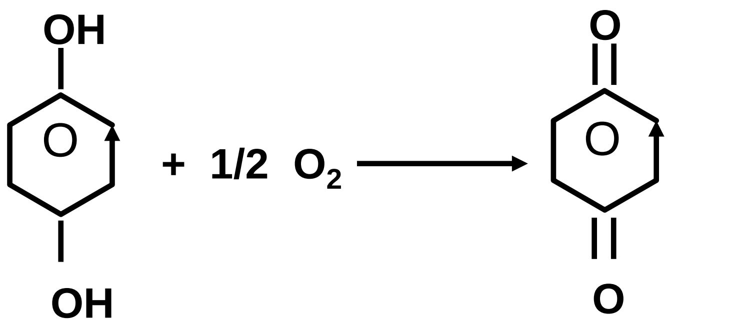
  RESIDUAL N_2H_4 AT ECONOMIZER INLET

Hydrazine

- **<u>ADVANTAGES:</u>**
  - DOESN’T CONTRIBUTE TO TDS
  - TRUE RESIDUAL TEST

- **<u>DISADVANTAGES:</u>**
  - POOR REACTIVITY WITH LOW TEMPERATURE
  - EXPENSIVE COMPARED TO SULFITE
  - **SUSPECT CARCINOGEN**
  - REQUIRES SPECIAL HANDLING / FEED EQUIPMENT
  - DECOMPOSES TO NH_3 WHICH CAN LEAD TO COPPER CORROSION

Hydroquinone



Hydroquinone Benzoquinone

- **REACTION:**
  - $C_6H_6O_2 + 1/2O_2 \longrightarrow H_2O + C_6H_4O_2$
- **CONTROL LIMITS:**
  - DISSOLVED OXYGEN TEST
  - TYROSINE AND LEUCO CRYSTALS VIOLET TEST
  - IRON REDUCTION TEST

Hydroquinone

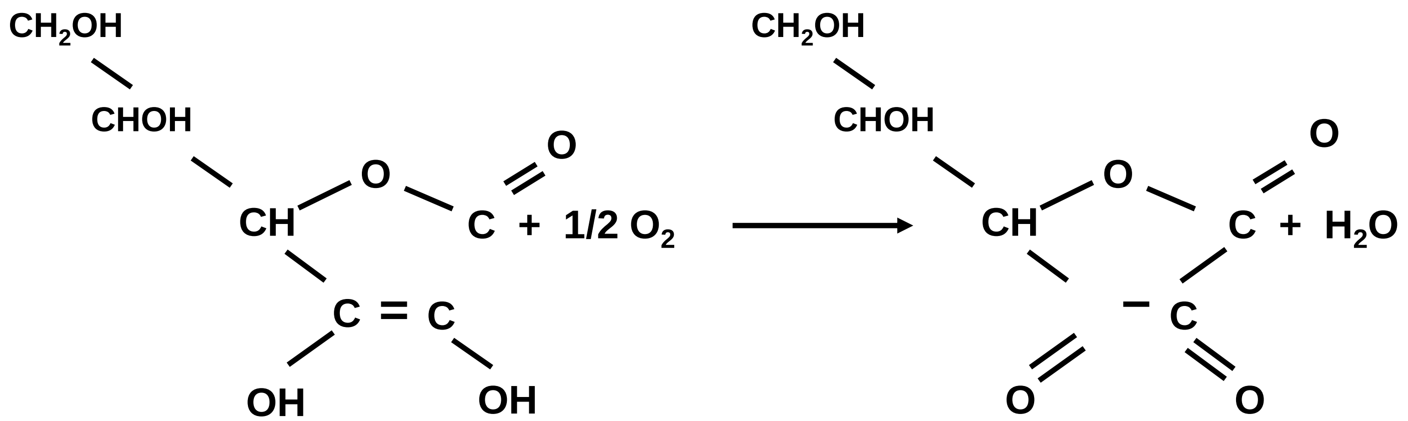
ADVANTAGES:

- DOESN’T CONTRIBUTE TO TDS
- REACTS FASTER THAN HYDRAZINE AT LOWER Temp
- DOESN’T REQUIRE SPECIAL HANDLING
- GOOD FOR LAY-UP
- NOT CARCINOGENIC

DISADVANTAGES:

- MORE EXPENSIVE THAN HYDRAZINE
- CAN INCREASE CATION CONDUCTIVITY

Ascorbic acid



Ascorbic Acid Dehydroascorbate

- **REACTION:**
  - $C_6H_8O_6 + 1/2O_2 \longrightarrow C_6H_6O_6 + H_2O$
- **CONTROL LIMITS:**
  - DISSOLVED O_2 TEST
  - IRON REDUCTION TEST

Ascorbic acid

ADVANTAGES:

- WORKS WELL IN pH RANGE (7-11)
- CONTRIBUTES NO TDS
- OXYGEN SCAVENGING

DISADVANTAGES:

- COST PER Kg is HIGH
- IS NOT THERMALLY STABLE
- NON-VOLATILE PRODUCT (ACIDIC)
- ATTEMPERATE WITH CAUTION
- DECOMPOSITION OF ACIDIC PRODUCTS MAY END UP IN CONDENSATE CIRCUIT

Diethyl hydroxylamine (DEHA)

$$4\,(CH_3CH_2)_2N\text{-}OH + 9\,O_2 \longrightarrow 8\,CH_3\text{-}C(=O)\text{-}OH + 2N_2 + 6H_2O$$

Diethyl Hydroxylamine — Acetic acid

$$\underset{\text{DEHA}}{2(C_2H_5)_2NOH} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Nitrone}}{2(C_2H_5)CH_3\,CHN{=}O} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\text{Nitrone}}{2(C_2H_5)CH_3CHN{=}O} + \underset{\text{Water}}{2H_2O} \longrightarrow \underset{\text{Ethylhydroxylamine}}{2C_2H_5HNOH} + \underset{\text{Acetaldehyde}}{2CH_3CHO}$$

$$\underset{\text{Ethylhydroxylamine}}{2C_2H_5HNOH} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Acelaloxime}}{2CH_3CH{=}NOH} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\text{Acetaloxime}}{CH_3CH{=}NOH} + \underset{\text{Water}}{H_2O} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + NH_2OH$$

$$4NH_2OH + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Nitrogen}}{2N_2} + \underset{\text{Water}}{6H_2O}$$

$$\underset{\text{Acetaldehyde}}{2CH_3CHO} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Acetic acid}}{2CH_3COOH}$$

Diethyl hydroxylamine (DEHA)

ADVANTAGES:

- No solids contribution to the boiler
- Steam volatile magnetite promoter
- Simple to dose and control
- Effective oxygen scavenger

DISADVANTAGES:

- Cost per kg is high
- Is not thermally stable
- Non-volatile product (acidic)
- Decomposition of acidic products may end up in condensate circuit

ORGANIC OXYGEN SCAVENGERS

ADVANTAGES

- No solids contribution to the boiler
- Steam volatile magnetite promoter
- Simple to dose and control
- Effective oxygen scavenger

DISADVANTAGES

- all organic oxygen scavengers contribute to cation conductivity
- all organic oxygen scavengers potentially decompose into acid species (organic acids)

Performance Criteria for Oxygen Scavenger

- The scavenger itself does not react corrosively with materials of construction and does not lower the pH to corrosive levels (pH < 8).
- Its reaction with oxygen is as rapid as possible, particularly in systems with high flow rates.
- The scavenger promotes the formation of passivating metal oxide films.
- Reaction products with oxygen are not corrosive.
- Dissolved solids contribution avoided.
- The scavenger should not interfere with the action of other treatment chemicals.
- It should not be toxic and much safer and easy to handle.
- It should be economical.

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Carbohydrazide

$$NH_2-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NH-NH_2 + 2\ O_2 \longrightarrow CO_2 + 2N_2 + 3H_2O$$

Indirect reaction

- $(N_2H_3)2CO + H_2O \xrightarrow{>135°C} 2\ N_2H_4 + CO_2$
- $2\ N_2H_4 + 2\ O_2 \longrightarrow 4\ H_2O + 2\ N_2$

Decomposition

- $(N_2H_3)2CO + H_2O \xrightarrow{>200°C} 2\ NH_3 + N_2 + H_2 + CO_2$
- 1 ppm Carbohydrazide liberates
  - 15 ppb NH_3
  - 14 ppb CO_2

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Carbohydrazide

- An oxygen scavenger that contributes no inorganic solids to the feed water or boiler water
- An oxygen scavenger that DOES NOT decomposes in organic acid species
- Contributes to passivation
- Controls oxygen corrosion

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Carbohydrazide

The byproducts and the percentage carbon content of oxygen scavengers in the table clearly illustrates that the byproducts of carbohydrazide contain no harmful organic compounds or acids [CEGB Report V 14, 1991].

On the basis of above data and its wide application in different power houses internationally as well as locally Carbohydrazide was selected for the evaluation.

Chemical/Formula	% C (wt.)	Reaction and/ Breakdown Products
Hydrazine N_2H_4	0	Nitrogen, Water, Ammonia
Cabohydrazide $(N_2H_3)_2CO$	13.3	Hydrazine, Nitrogen, Water, Ammonia Carbon Dioxide
Erythrobic acid $C_6H_8O_6$	40.9	Dihydroascorbic acid Salts of Lactic and Glycolic Carbon Dioxide
Diethylhydroxylamine $(CH_3CH_2)_2NOH$	53.9	Acetaldehyde Acetic acid Acetate ion Dialkylamines Ammonia Nitrate Nitrite
Methylethylketoxime $(CH_3)(CH_3CH_2)C{=}NOH$	55.2	Methylethylketone Hydroxylamine Nitrogen Nitrous Oxide Ammonia Carbon Dioxide
Hydroquinone $C_6H_4(OH)_2$	65.5	Benzoquinone Light Alcohols Ketones Low Molecular Weight Species Carbon Dioxide

OBJECTIVES

- To evaluate the suitability and efficiency of carbohydrazide as an alternative oxygen scavenger to hydrazine in the high-pressure boiler.

- To determine the consequences of degradation by-products on boiler system.

- To evaluate the ability of the alternative oxygen scavenger in forming and maintaining an oxide film in the boiler.

- To evaluate whether the alternative oxygen scavenger is generating any negative effects on the efficiency of the boiler.

EXPERIMENTAL

- Two boilers # 81 and # 82 of Phase–II at Al-Jubail Plants, each generating 130 MW/h, were selected for the trial tests in consultation with chemical manufacturing company.

- Boiler # 81 was run with carbohydrazide and boiler # 82 with hydrazine. Both these boilers are pressurized box type water tube boilers. The maximum continuous rating (MCR) of steam is 710 tons/h.

Test Conditions (Boiler chemistry)

Parameters/ Samples	Condensate	Daerator out	Feed Water/ Economizer inlet	Boiler Blow Down (Drum)	Saturated Steam
pH	8.5 – 9.2	-------	8.7 – 9.2	9 – 9.8	8.7 – 9.2
Sp. Conductivity (µS/cm)	<3	-------	<3	<50	<3
Cat. Conductivity (µS/cm)	<0.5	-------	-------	-------	<0.5
Copper (ppb)	<5	--------	<5	<20	----
Ammonia (ppm)	<0.3	-------	<0.3	-------	<0.3
Iron (ppb)	<10	------	<10	<50	------
Dissolved O_2 (ppb)	<20	<10	Nil or <7	------	------
Hydrazine (ppb)	------	-------	10 - 20	------	------
Silica (ppb)	<20	-------	<20	1000	<20
Sodium (ppb)	<10	-------	<10	------	<10
Chloride (ppm)	<0.01	-------	<0.05	<0.5	<0.05
Phosphate (ppm)	------	-------	-------	5 - 10	------
P-Alkalinity(ppm)	------	-------	-------	<5	------
M-Alkalinity(ppm)	------	-------	-------	<15	------

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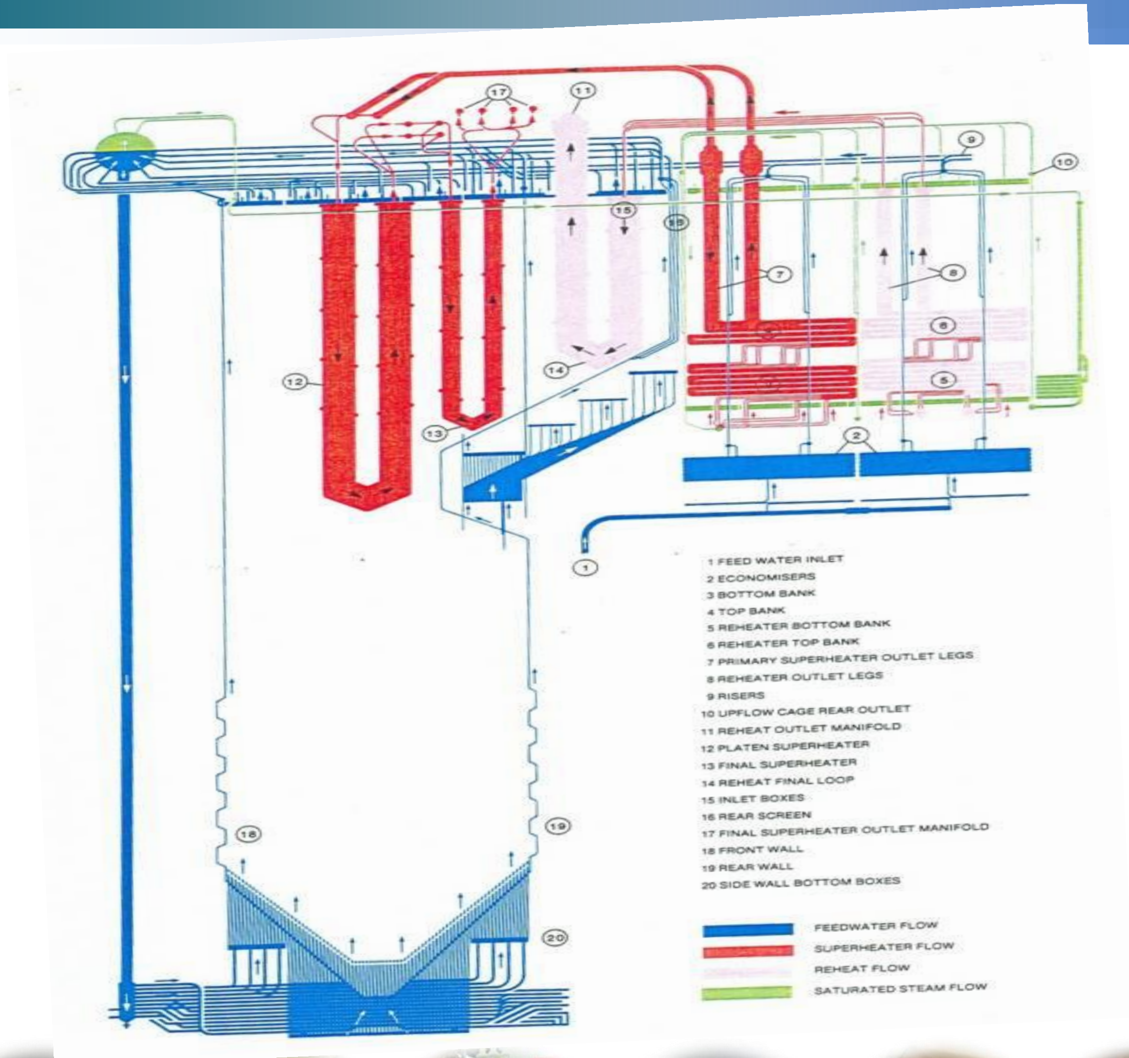
Test Conditions (Operations)

S. No.	Equipment	Capacity	Water/Steam		
			Pres. (Bar)	Temp. ^0C	Flow M^3/H
1	Condensate	----------	9.5-9.8	99-121	----
2	Deaerator	86 M^3	5	156	700
3		25 M^3	----	---	----
4	Boiler feed Pump	900 M^3	103	----	697
5	HP Heater 1	----	103	160-195	697
6	HP Heater 2	-----	103	195-233	697
7	Economizer	-----	102	230-295	700
8	Boiler	12 1M^3	104	310	700
9	Super heater	39 M^3	95	515	700
10	Hydrazine tank pump	560 L	150	----	50L/H
11	Phosphate tank pump	560 L	150	--------	50L/H

TYPICAL BOILER SHOWING WATER AND STEAM FLOW



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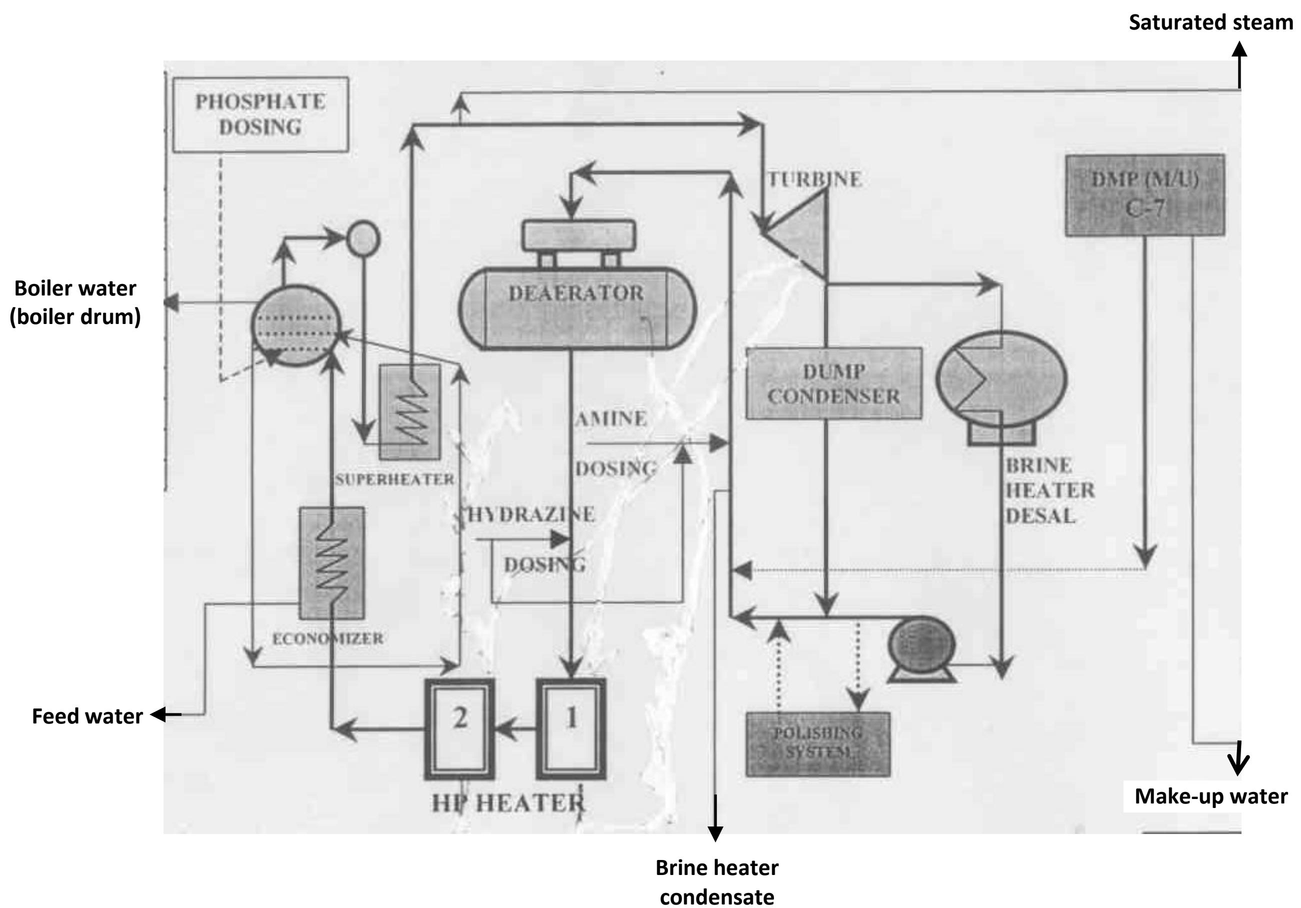
BOILER WATER CYCLE AND SAMPLING POINTS

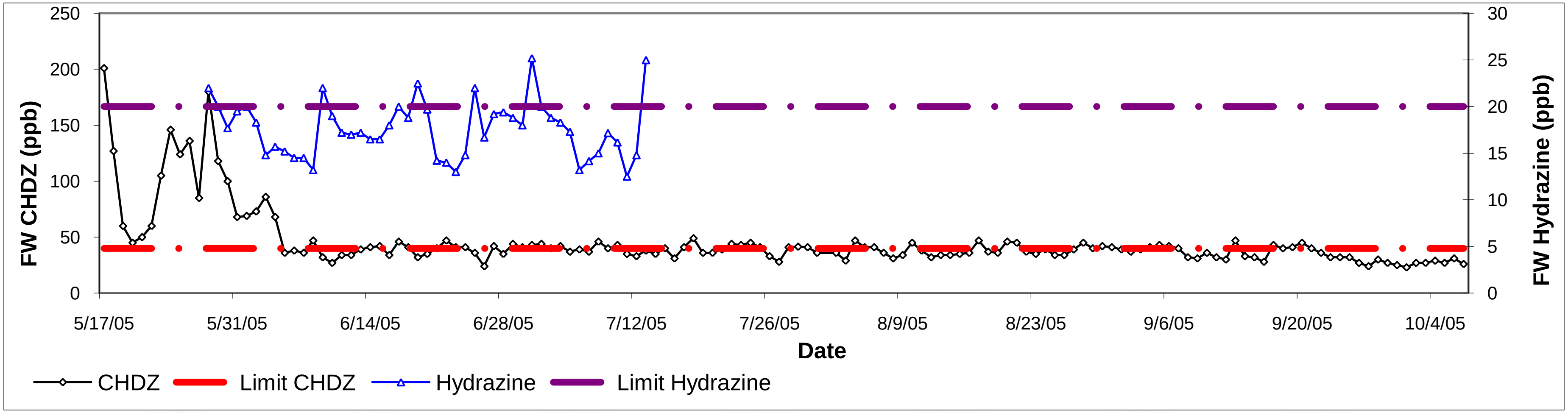


RESULTS AND DISCUSSIONS

Optimization of Carbohydrazide

Chemical feed rates for hydrazine were established to maintain hydrazine residual around 20 ppb in feed water.

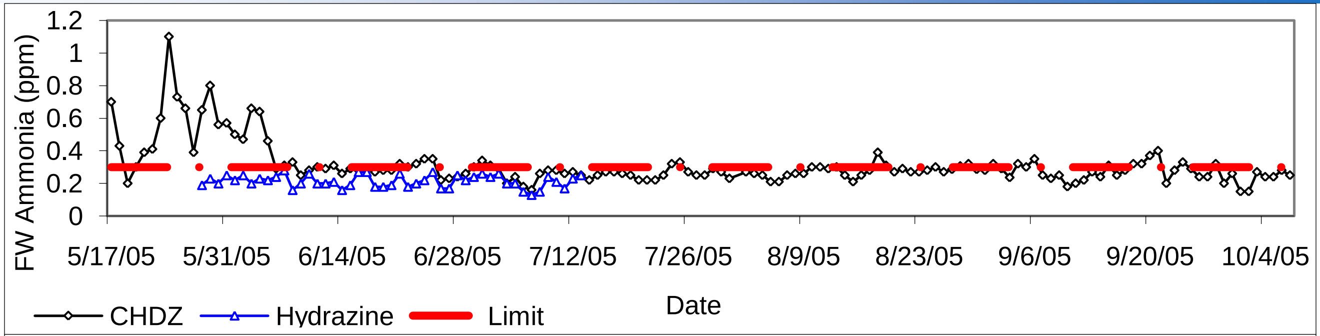
At the start with the recommended dosage of 1.5 ppm of carbohydrazide, determination of carbohydrazide in feed water was observed to give inconsistent values. The inconsistency observed was attributed to the high temperature of the feed water (235^{o}C) because at temperatures above 150^{o}C carbohydrazide hydrolyzes to hydrazine.

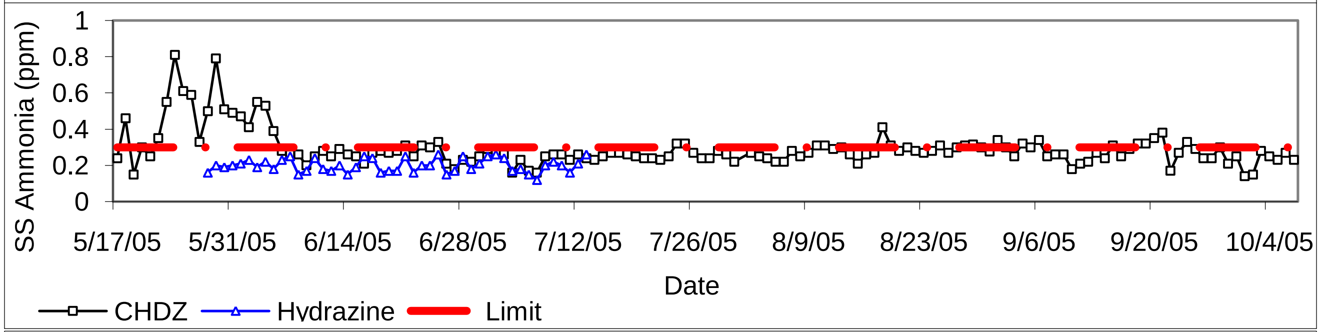


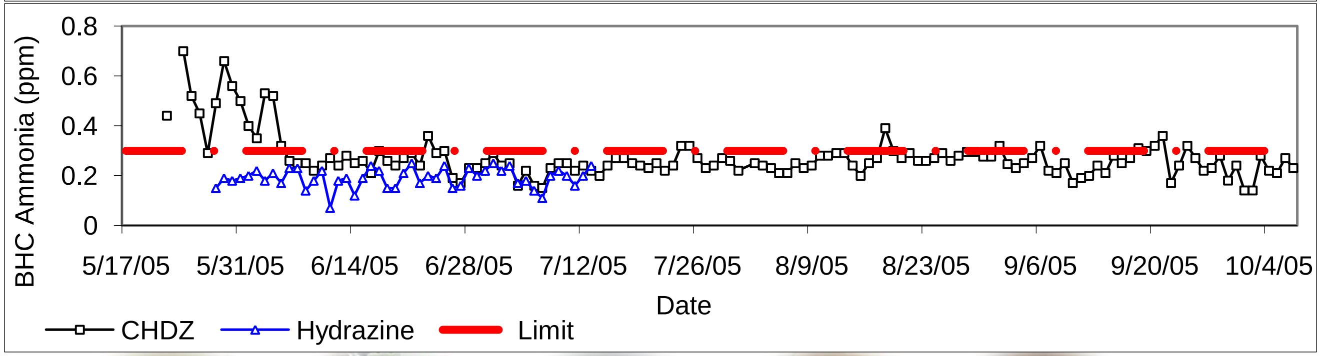
Optimization of Carbohydrazide

At the start with the recommended dosage of 1.5 ppm of carbohydrazide, high values for ammonia and copper were recorded.

The dose rate was later reduced from 1.5 to 0.7 ppm till the parameters (copper & ammonia) were maintained within the normal range and stabilized.



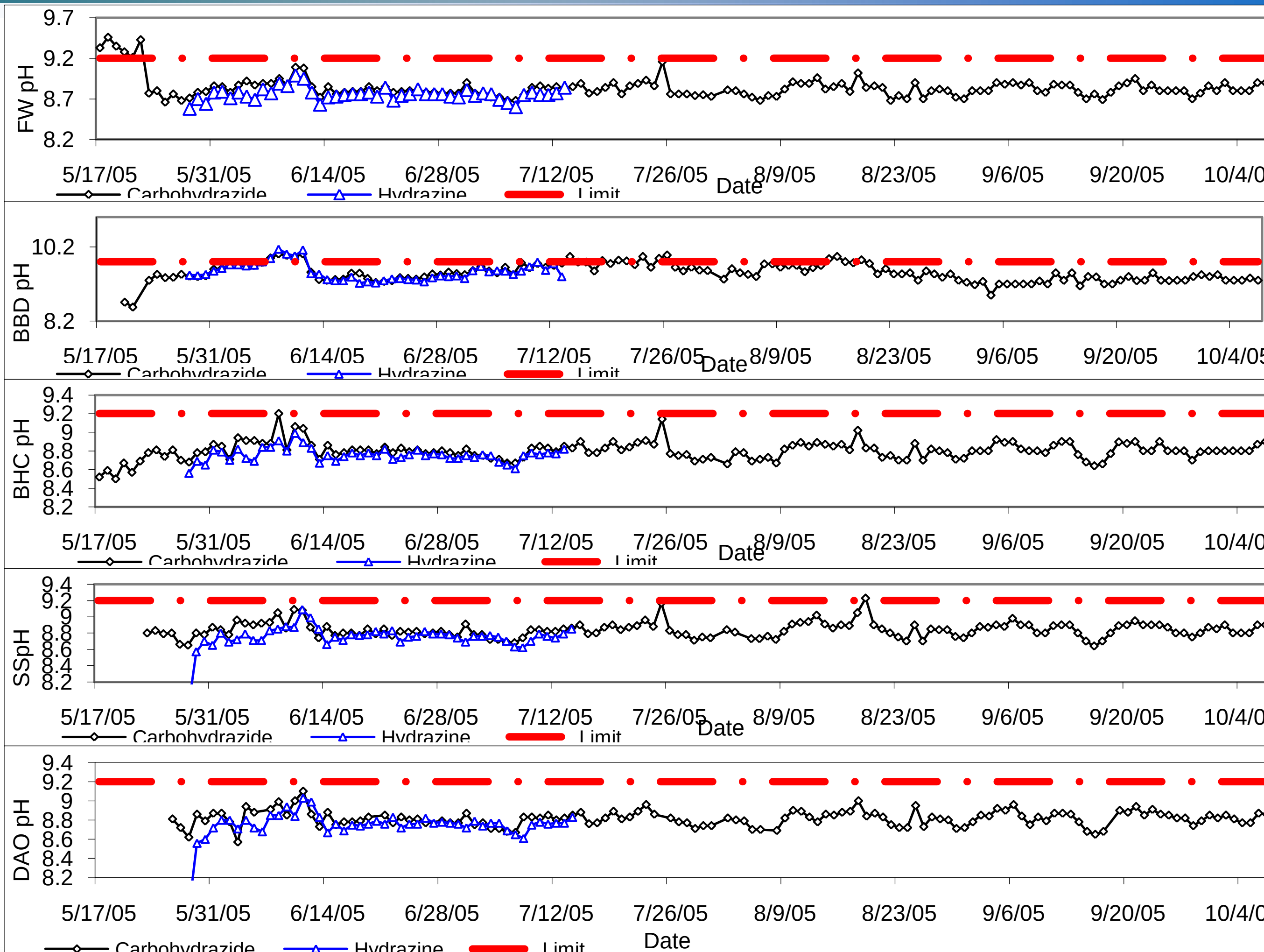




Boiler Chemistry

pH Control

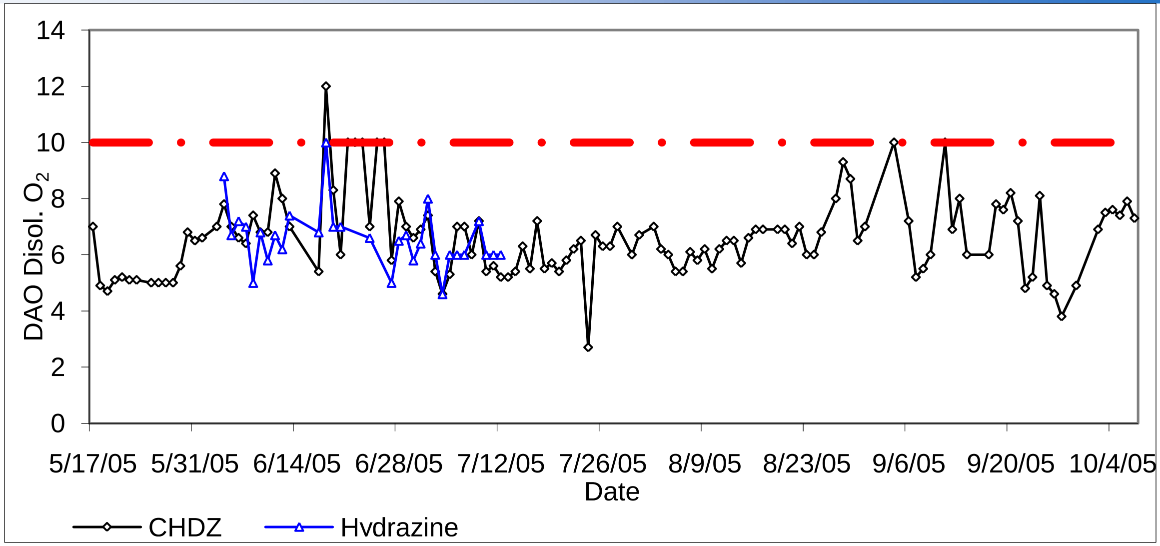
pH values for both hydrazine and Carbohydrazide were found to be maintained in the range of 8.6 and 9.0 for Brine heater condensate (BHC), Feed water (FW), Saturated steam (SS) and Deaerator outlet (DAO) whereas for Boiler blow down (BBD) it was in the range of 9.0 and 10.

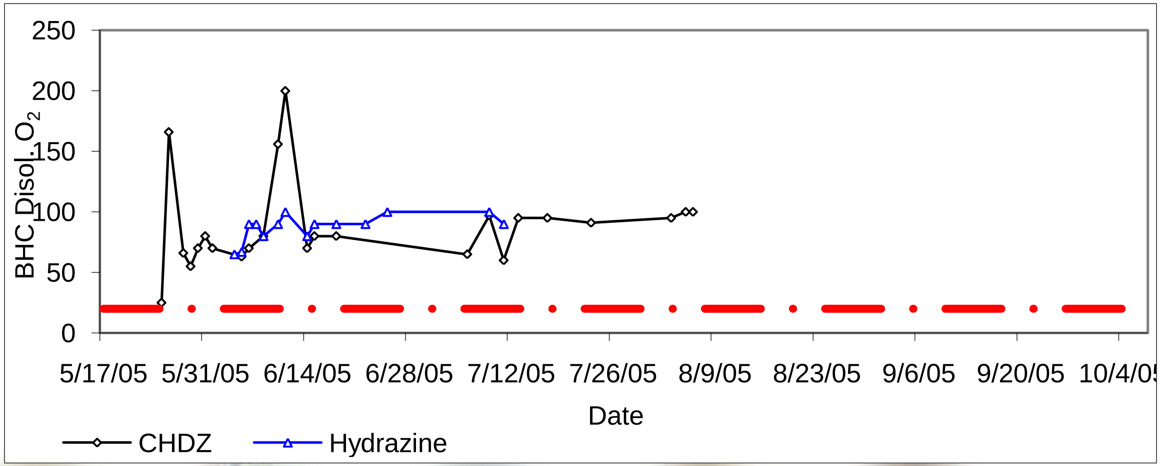


Boiler Chemistry

Dissolved Oxygen

Average dissolved oxygen with both hydrazine and Carbohydrazide in the DAO was found to be ≤ 7 ppb, whereas in the BHC it was found to be high at an average of 87 ppb. This was attributed to the air leakage.



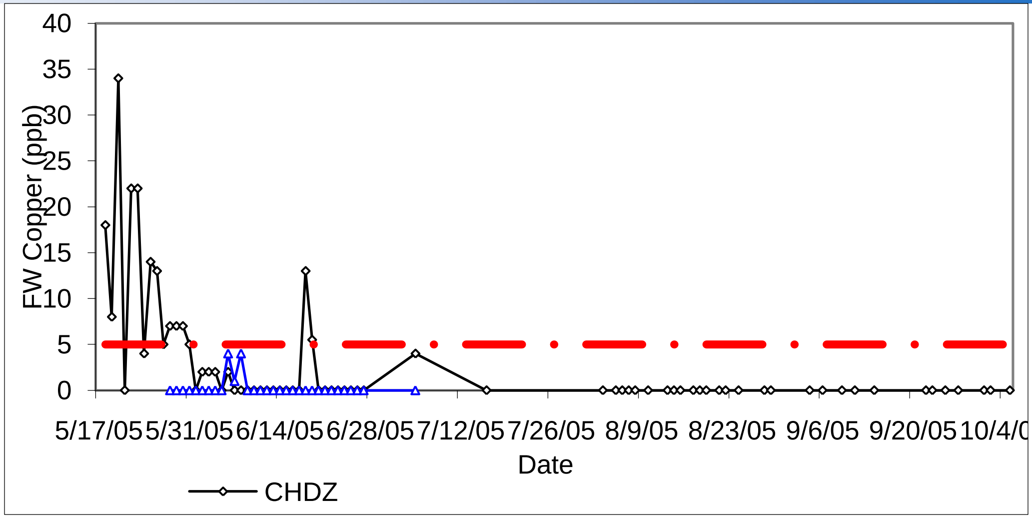


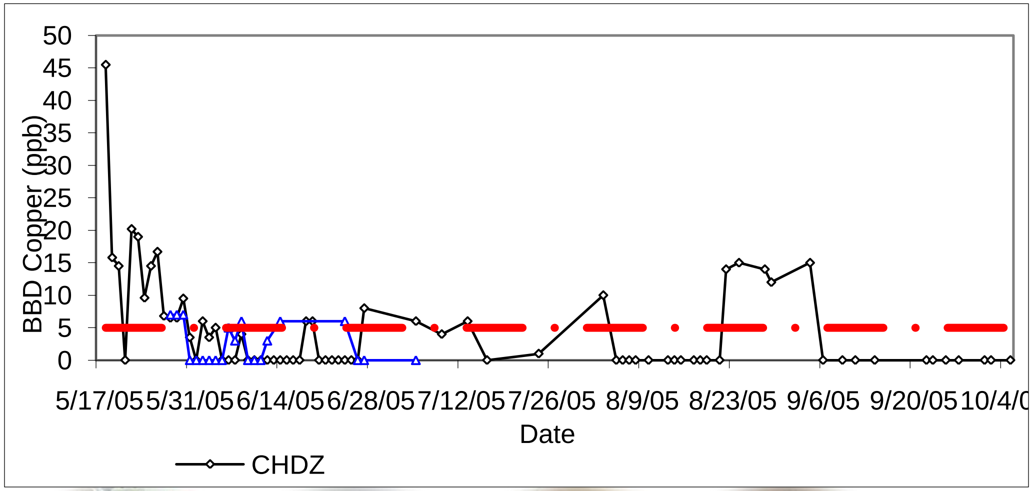
Boiler Chemistry

__Control of Copper levels__

With hydrazine, the average concentrations for copper in feed water was found to be 3 ppb and in boiler water it was found to be 6 ppb, whereas with carbohydrazide dosing, the average concentrations for copper in feed water was found to be 3 ppb and in boiler water it was found to be 4 ppb.

This showed that copper levels in feed water were maintained at the baseline value whereas a 33% reduction was found in the boiler water (drum).



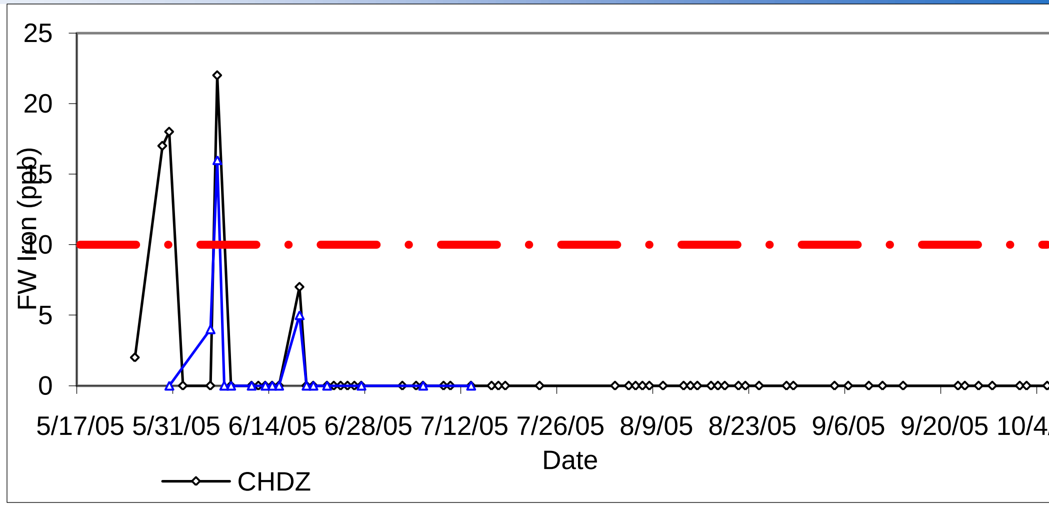


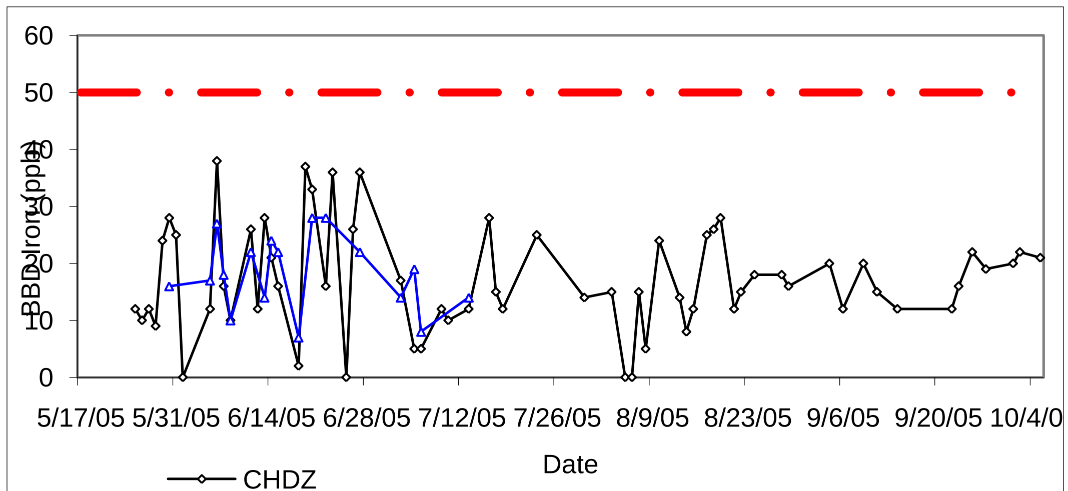
Boiler Chemistry

Control of Iron levels

With hydrazine, the average concentrations for iron in feed water was found to be 8 ppb and in boiler water it was found to be 19 ppb whereas with carbohydrazide dosing, the average concentrations for iron in feed water was found to be 2 ppb and in boiler water it was found to be 17 ppb.

This showed a reduction of iron levels in the feed water by 75% and in the boiler water (drum) a reduction of 10%.





Corrosion studies

The exposed coupons were visually examined. A uniform and non-porous oxide film was found to be adhered on the coupons indicating the protective nature of the films. The corrosion rate of 0.044 mpy determined for carbon steel coupons fixed in drum at water side with hydrazine dosing indicates extremely low corrosion.


Coupons in Boiler Drum Before test

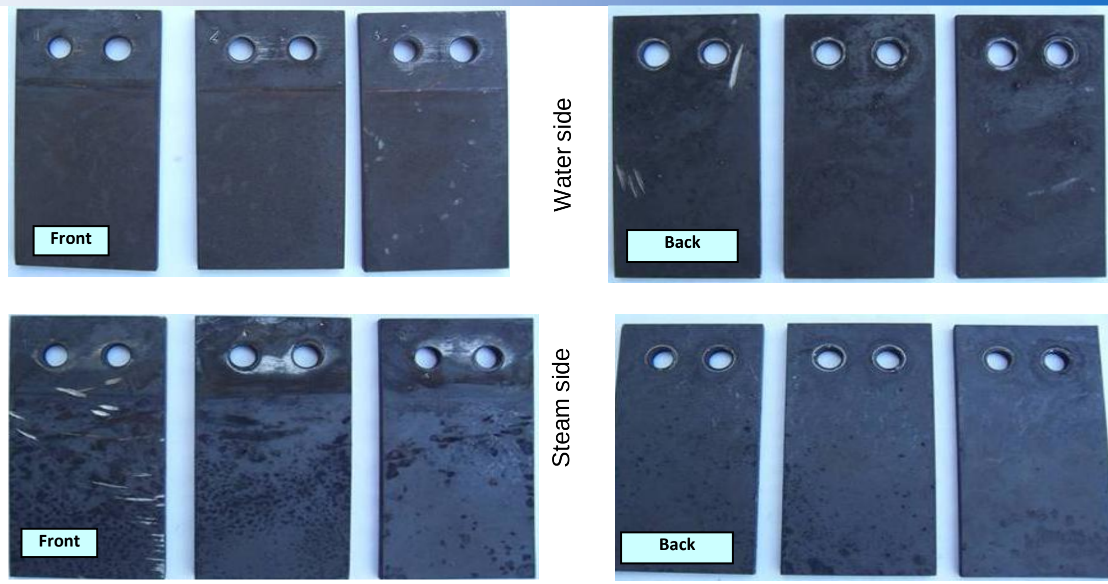

Coupons in Boiler Drum after test


Coupons in HP heaters Before test

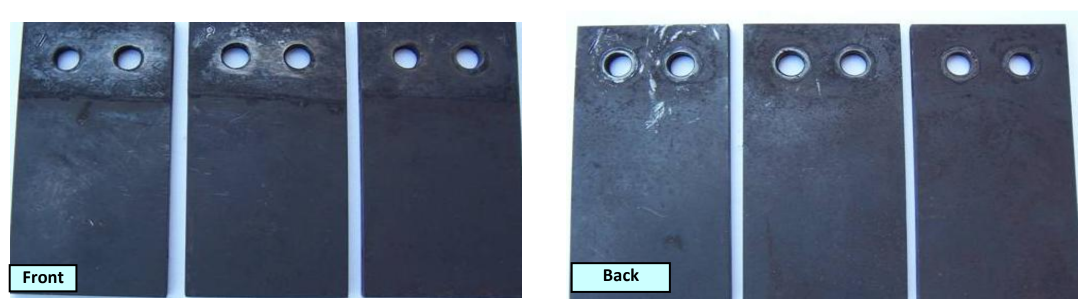

Coupons in HP heaters after test

Corrosion studies

The corrosion rates determined with carbohydrazide dosing for carbon steel coupons fixed in drum at water side and steam side were 0.384 mpy and 0.444 mpy respectively, whereas that determined for carbon steel and 70/30 cupronickel in HP heaters were 0.251 mpy and 0.128 mpy respectively. The corrosion rates of the material appear to be low and effect of corrosion appears to be insignificant.



Carbon steel coupons after exposure in water drum under Carbohydrazide dosing boiler #81



Cupronickel coupons after exposure in HP heater under Carbohydrazide dosing boiler #81

CONCLUSIONS

- The results indicated the suitability and efficiency of Carbohydrazide oxygen scavenger as an alternative to hydrazine in SWCC high pressure boiler provided the concentration of residual hydrazine (decomposition by-product of Carbohydrazide) is maintained at levels between 30-40 ppb in the feed water.

- No harmful degradation by-products were found.

- Carbohydrazide was found to be a good oxygen scavenger at a concentration dose rate of 0.7ppm.

- Optimized dose rate resulted in maintaining the boiler chemistry within design limits.

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CONCLUSIONS

- Iron levels measured at economizer inlet (boiler feed water) were reduced by 75% whereas for copper it was found to be maintained at the baseline value. In the boiler water (drum) the reduction in Fe and Cu were 10% and 33%, respectively.

- The corrosion rates indicated very little or negligible corrosion due to either hydrazine or Carbohydrazide. However hydrazine showed much lower rates compared to Carbohydrazide.

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Acknowledgment

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Thank You !

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