GOOD BOILER OPERATIONAL PRACTICES

Boiler water management

MAKE UP WATER TREATMENT

- High pressure boilers need low TDS & low silica water.
- Low TDS is for preventing deposits
- Low silica is for limiting silica carryover with steam to turbine.
- DM plants are used for bringing down the conductivity to less than 0.5 micro mho /cm & silica below 0.02 ppm.
- Suspended solids, organic matter, turbidity are removed pretreatment plants such as chlorination, coagulation, clarification & filtration.


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Boiler Internal corrosion due to water chemistry

- Corrosion due to low pH or high pH.
- Corrosion due to deposits
- Corrosion due to Oxygen

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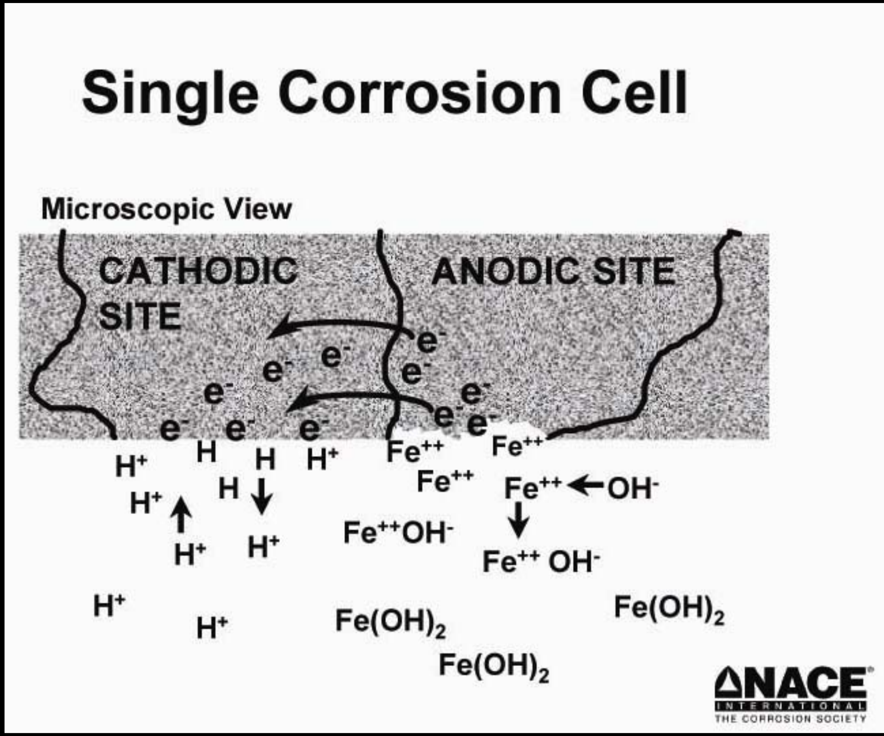
What happens when the pH is low in a low pressure / low temperature system

- The H^+ ions in water are more when pH is low. The hydrogen ions are ready to acquire electrons from metal. Hence the Fe^{++} ions break away from the Fe- FeC structure of steel.



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What happens when the pH is low and in high pressure / high temperature system

- HYDROGEN WHEN PRESENT DIFFUSES THROUGH THE GRAIN BOUNDARIES AND CAUSES INTERGRANULAR CRACKS AND AT TIMES BLOWS A

  METAL PIECE OUT.

HYDROGEN DAMAGE CAN OCCUR UNDER FOLLOWING CONDIITONS

- LOW pH WATER PRESENT IN STRESSED ZONE- STRESS CORROSION CRACKING
- LOW pH WATER PRESENT BENEATH DEPOSITS.

REACTIONS OF HYDROGEN IONS WITH METAL

- $4H + Fe_3C$ (pearlite) = CH_4 + Fe (ferrite)
- The hydrogen ions being small in atomic diameter easily travels along boundary and causes methane formation on heating. Methane expands and leads to inter-granular crack.

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Pre-boiler system corrosion

- When the pure steam condenses the pH is close to 7. This disturbs the magnetite layer and generates loose iron.
- When there is a chance for presence of CO2 in condensate the carbonic acid leads to corrosion.
- A pre boiler system may consists open tanks which may corrode due to Oxygen.

Protection against Pre-boiler system corrosion

- Amine based feedwater chemical is added which improves the pH of condensate and thus avoids the corrosion.
- When DM water pH is close to 7, it should be boosted at DM plant outlet / or else complete tank & piping should be rubber lined / made of Stainless steel.

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Damages due to pre-boiler system corrosion

- Adds suspended solids to boiler feedwater which leads to foaming in boiler drum and thus carryover.
- Accumulates at surface irregularities such as weld joints and work as sites for corrosion.
- Leads to pH – PO4 fluctuations on load change.
- Leads to porous deposits beneath which either pin holes develop or hydrogen damage can occur.


If left untreated, oxygen in the feedwater can cause severe pitting in system tubing, especially in the low-temperature pre-boiler section.

Water carryover due to suspended solids

What happens when O_2 is available?

- In the presence of oxygen, iron becomes Rust.
- Rust is the common name for a very common compound, iron oxide, Fe_2O_3, is common because iron combines very readily with oxygen -- so readily, in fact, that pure iron is only rarely found in nature.

PROOF OF CARRYOVER-DEPOSISTS INSIDE SUPERHEATER TUBE

The reaction is one where the iron is oxidized at the anode and released into the water . The electrons from oxidation are then released and absorbed by oxygen at the cathode . The reaction is :

Anode:	$Fe^{\circ} \rightarrow Fe^{++} + \ + 2e^{-}$
Cathode:	$\frac{1}{2} O_2 + H_2O + 2e^{-} - \rightarrow 2OH^{-}$
Electrochemical Reaction:	$Fe^{\circ} + \frac{1}{2} O_2 + H_2O \rightarrow Fe(OH)_2$

As this reaction continues , due to the presence of free oxygen m a corrosion cell is formed which eventually forms the classic oxygen pit.

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On the other hand, where an oxygen scavenger is properly used in the system to eliminate free reactive oxygen , and where elevated temperatures exist. The ferrous hydroxide [$Fe(OH)_2$] is converted to a dense protective film referred to as magnetite (Fe_3O_4).This magnetite forms a protective film on the reactive surfaces, protecting the metal from attack from water and oxygen. The reaction is:

$$Fe(OH_2) \rightarrow Fe_3O_4 + H_2 + 2H_2O$$

Once this film is formed, the scavenging of oxygen is important, because free oxygen can react to revert the magnetite into iron oxide (hematite) which is porous.

$$\underbrace{2Fe_3O_4}_{\text{magnetite}} + \tfrac{1}{2}\,O_2 \rightarrow \underbrace{Fe_2O_3}_{\text{hematite}} + H_2O$$

With reversion to iron oxide, you will see a reddish coating on the tubes and returned potential for oxygen pitting. Thus, it is very important that you scavenge the oxygen in the system at all times.

Thermal Deaeration

- Deaerator is used to raise water temperature close to boiling point. The scrubbing action of steam on water droplets strips the O_2 & CO_2 and lets it through the deaerator vent.

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Underlying principle of deaeration

The solubility of a gas in a liquid is expressed by HENRY's LAW.

THE EQUILIBRIUM CONCENTRATION OF A GAS DISSOLVED IN A LIQUID IS PROPORTIONAL TO THE PARTIAL PRESSURE OF THAT GAS WHICH CONTACTS THE LIQUID.

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Henry's law

- $C_{total} = k P$
- Where,
- C_{total} = total concentration of gas in the solution
- P = pressure of gas above the solution
- k = a proportionality constant known as Henry's law constant.

How it works in a deaerator?

- In deaerator the space above water is filled with steam and continuously some steam is vented out.
- Since the concentration of gases is less in the space above the water, the dissolved gas in water is less.
- Yet for effective stripping of gases, contact of water to steam should be done in the best possible manner.
- This is done by the spray nozzles, trays and scrubbers

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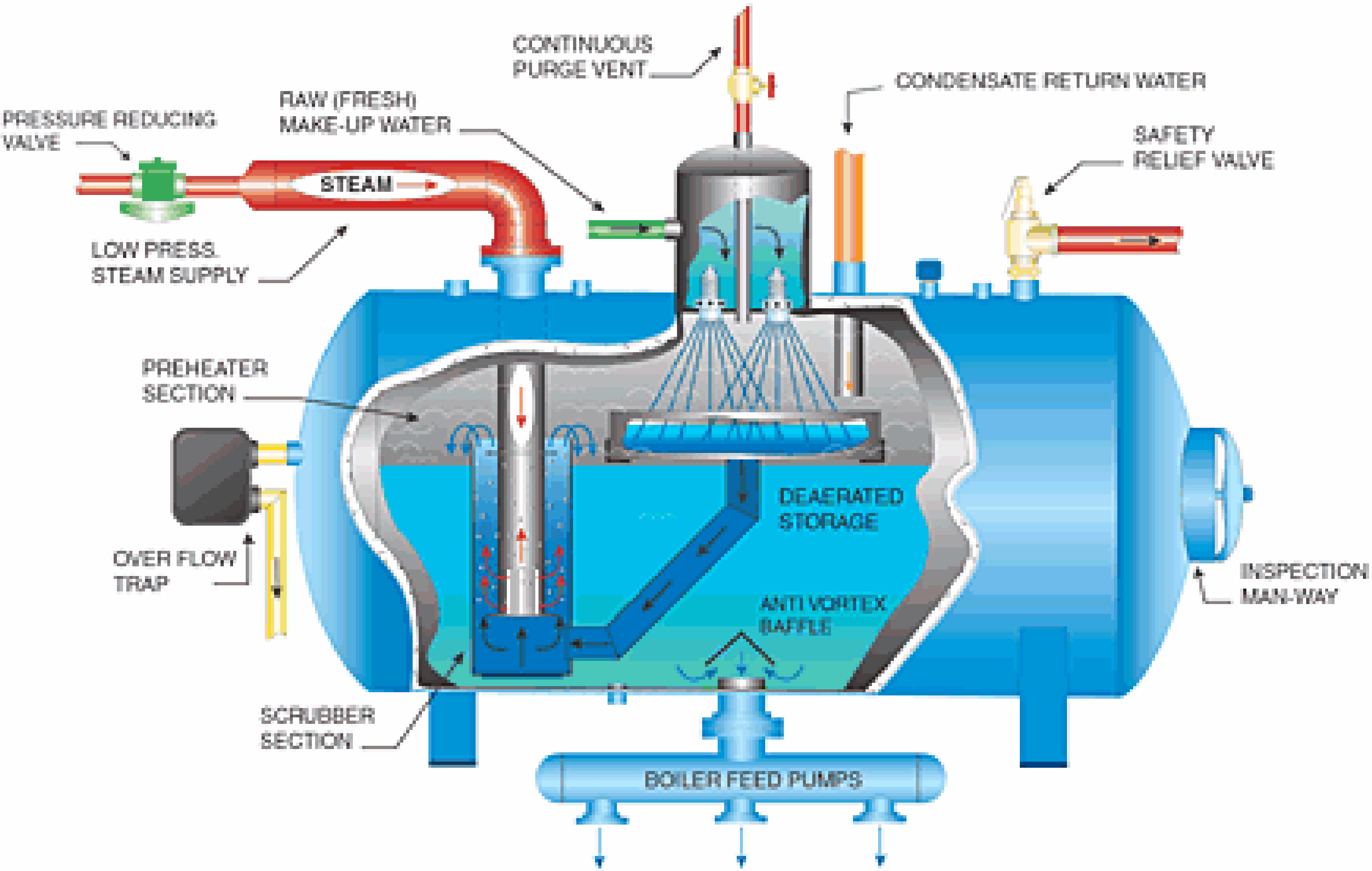
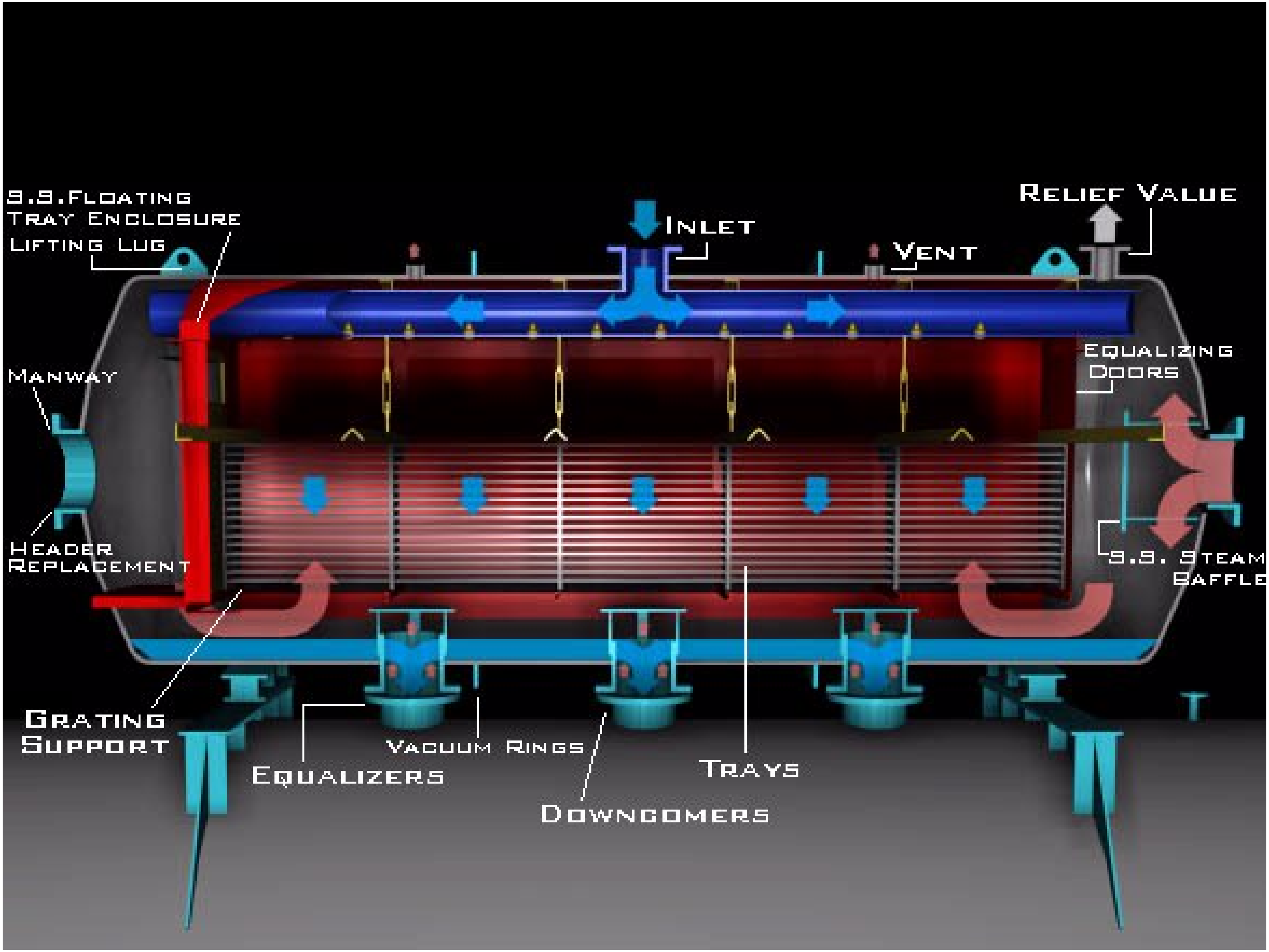
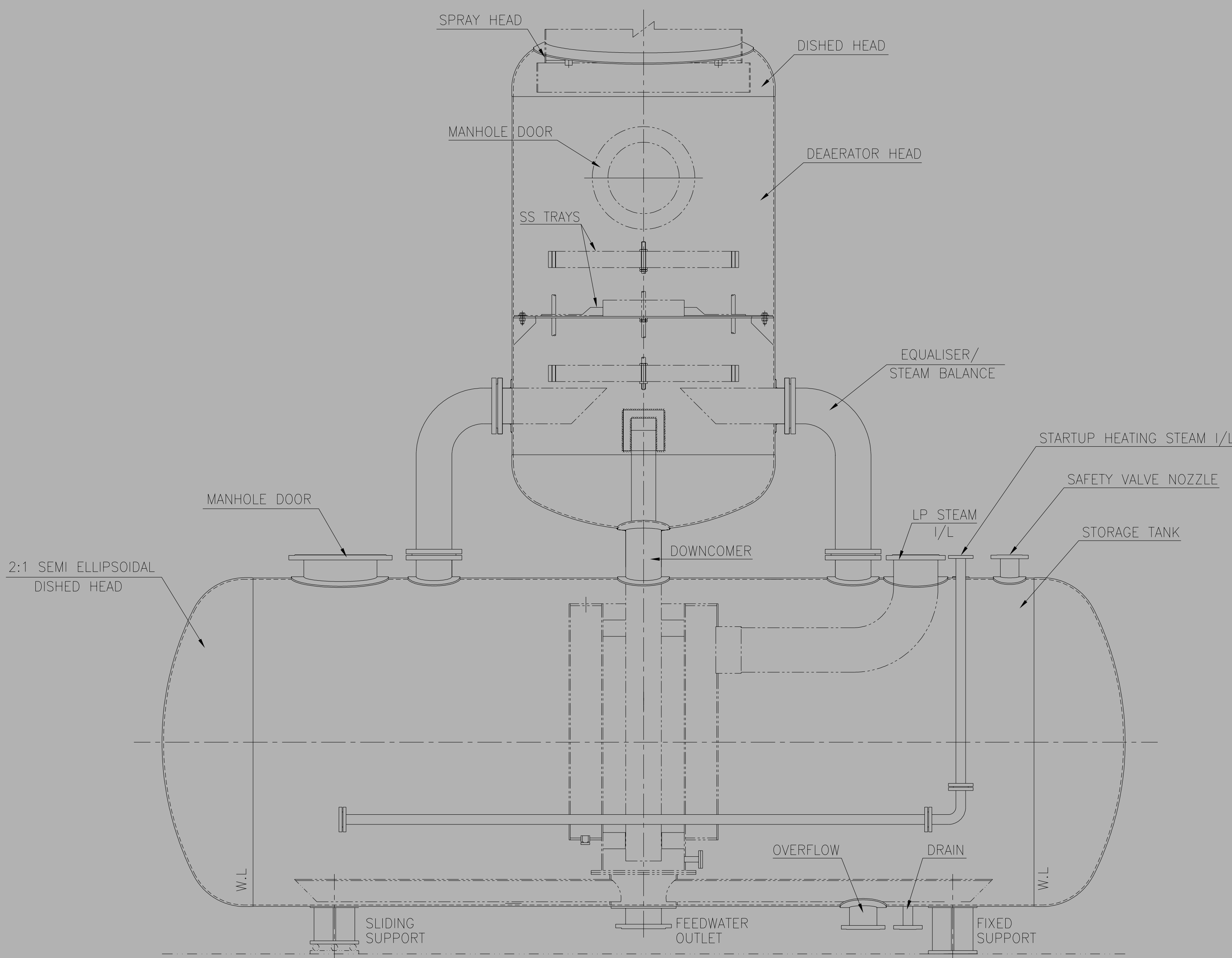
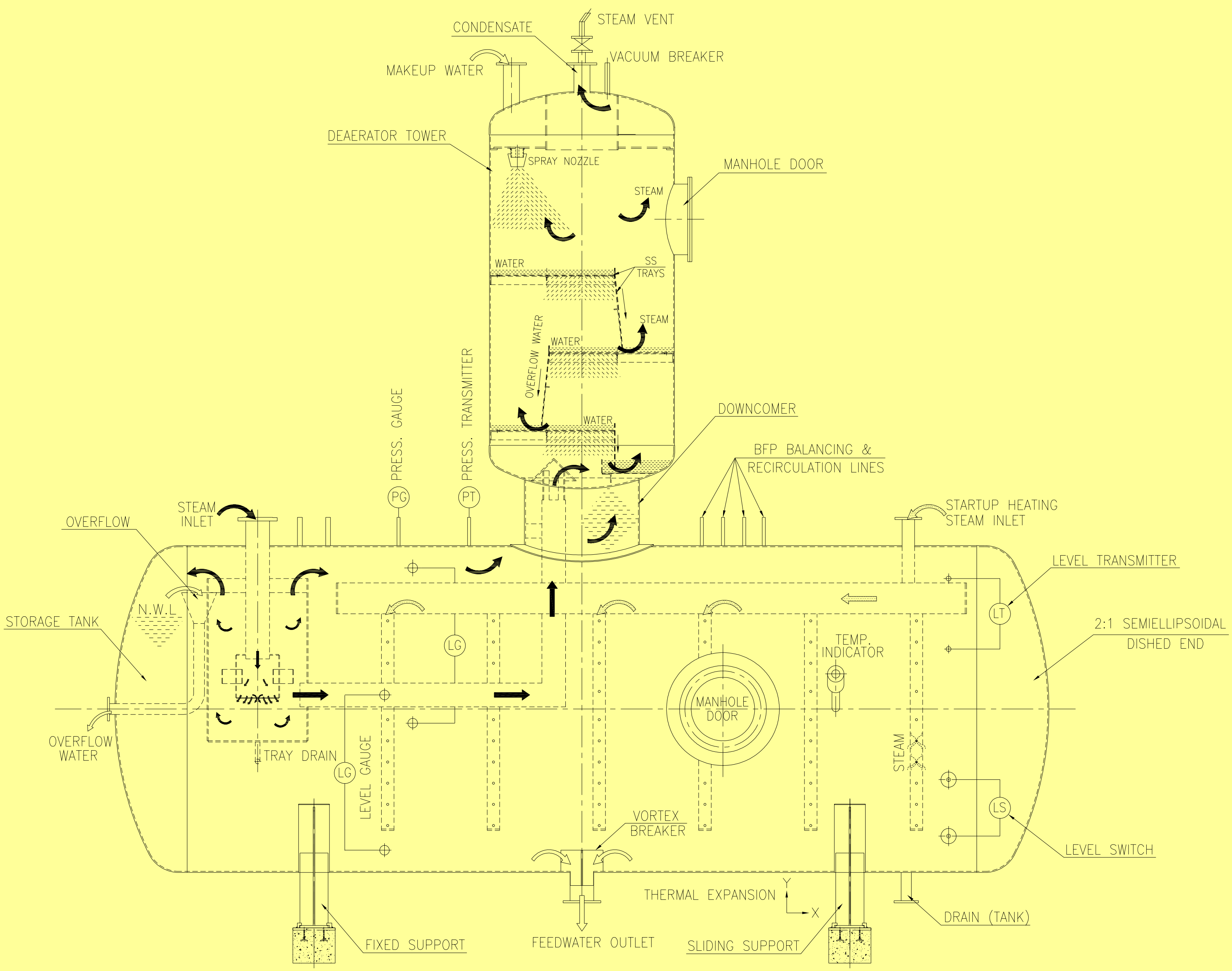

CONTINUOUS
PURGE VENT
CONDENSATE RETURN WATER
RAW (FRESH)
MAKE-UP WATER
PRESSURE REDUCING
VALVE
STEAM
SAFETY
RELIEF VALVE
LOW PRESS.
STEAM SUPPLY
PREHEATER
SECTION
DEAERATED
STORAGE
OVER FLOW
TRAP
INSPECTION
MAN-WAY
ANTI VORTEX
BAFFLE
SCRUBBER
SECTION
BOILER FEED PUMPS


S.S.Floating
Tray Enclosure
Lifting Lug
Inlet
Vent
Relief Value
Equalizing
Doors
Manway
Header
Replacement
S.S. Steam
Baffle
Grating
Support
Equalizers
Vacuum Rings
Downcomers
Trays

DEAERATOR AND STORAGE TANK ASSEMBLY



DEAERATOR AND STORAGE TANK ASSEMBLY



CHEMICAL DOSING

- To protect the boiler and accessory equipment from corrosion.
- Aim is to retain the integrity of magnetite layer that forms due to high temperature.

Mechanism of formation of magnetite

- Schikorr established

$$Fe + 2\ H_2O = Fe^{++} + 2OH^- + H_2$$

$$Fe^{++} + 2OH^- = Fe\ (OH)_2$$

$$3Fe(OH)_2 = Fe_3O_4 + 2H_2O + H_2$$

The magnetite layer

- Under good boiler operating condition, the oxidation of iron to magnetite forms a fine tightly adherent layer with good protective properties.
- As the thermal expansion coefficients matches with steel, the layer does not give way in varying heat flux.
- The layer gets disturbed due to presence of O2, High pH & low pH environment.
- The layer will be disturbed when there are mechanisms by which the chemical concentration takes place.

Common causes of corrosion is dissolved gases and the acidic water

- Dissolved gases depend on source of water
- Dissolved gases depend on addition of treatment chemicals such as chlorine.
- Dissolved gases such as oxygen and CO_2 are naturally occurring.

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EFFECT OF O2

- Oxygen Leads to localized pitting corrosion.
- At high temperature, even a small O2 leads to high rate of corrosion.
- When there is a deviation the failure is always at heaters or at economizers.

Chemical deaeration

- Mechanical deaerators can remove O_2 to a level of 0.005 ppm.
- Chemicals are to be added to ensure complete removal of O2.
- Always excess reserve of chemical is maintained.
- Chemical deaeration alone will be very costly.

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Chemicals used for O_2 removal

- Hydrazine – N_2H_4
- Reaction is as below:

$$N_2H_4 + O_2 = 2\ H_2O + N_2$$

- NITROGEN DOES NOT CORRODE UNLESS IT IS OXIDISED, WHICH DOES NOT HAPPEN IN WATER SIDE OF BOILER.
- RECOMMENDED FOR ALL HIGH PRESSURE BOILERS > 50 KG/CM2G

DECOMPOSITION OF HYDRAZINE

- Production of ammonia from excess hydrazine

$$3N_2H_4 \Longrightarrow 4NH_3 + N_2$$
$$2N_2H_4 \Longrightarrow 2NH_3 + N_2 + H_2$$

- ALKALINE AMMONIA (NH_4 OH) DOES NOT ATTACK COPPER / COPPER ALLOYS UNLESS OXYGEN IS PRESENT.
- AMMONIA NEUTRALISES CARBON-DI-OXIDE AND THUS REDUCES CONDENSATE LINE CORROSION.

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Hydrazine also protects boiler against corrosion by formation of magnetite layer

$N_2H_4 + 6\ Fe_2O_3 = 4\ Fe_3O_4 + N_2 + 2\ H_2O$

Hydrazine + Ferric oxide = magnetite oxide + nitrogen + water

About Hydrazine

- It is a toxic liquid and to be handled with care.
- It flashes at room temperature and hence 35% solution is made.
- Theoretically 1 ppm of hydrazine is required for every O2 ppm. But in practice higher ppm (30 times too) is required for reaction.

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Where to dose hydrazine?

- It would be ideal to dose the hydrazine at deaerated water storage tank through a distributing pipe.
- The reaction time taken by hydrazine is longer particularly at low temperature. To have the advantage of time deaerator would be the right place.
- It would also prevent the corrosion of deaerator.

Hydrazine should be handled with care since it is allergenic and carcinogenic to humans.

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Other Oxygen Scavengers

- Sodium sulfite – Na_2SO_3

- Reaction is as below:

$Na_2SO_3 + O_2 = 2Na_2SO_4$

- Cheaper as compared to Hydrazine
- Adds to dissolved solids in water
- Usable for boiler operating below 50 kg/cm2g

CARBOHYDRAZIDE $(N_2H_3)_2CO$-CHZ

This is the first hydrazine substitute designed to provide a product that acts like hydrazine but does not have the hazards contributed to hydrazine. The product is had a patent for use as an oxygen scavenger.

CARBOHYDRAZIDE (N2H3)2CO-CHZ

CHZ does not contribute to the boiler solids and reacts at a rate of 1.4 ppm of CHZ for every 1 ppm of oxygen. This however will also form an additional 0.7 ppm of CO_2, which will have to be taken into account when calculating the neutralizing amine requirement.

The material is usually sold as a 6.5% solution and is fed to the feed water system to be controlled at 0.05 to 0.3 ppm as Hydrazine. CHZ will decompose along the same lines as Hydrazine.

N,N-DIETHYLHYDROXYLAMINE ($(CH_3CH_2)_2NOH$) – DEHA

DEHA is a volatile oxygen scavenger, which is usually sold as an 85% or 25% liquid. It has the ability to passivate the metal surfaces in the boiler, then pass out the boiler with the steam, and act as a metal passivating agent in the return line system.

N,N-DIETHYLHYDROXYLAMINE (($CH_3CH_2)_2NOH$) – DEHA

DEHA can be catalyzed with either a copper salt or Hydroquinone. The feed rate of the DEHA s 1.24 ppm of DEHA for 1 ppm of oxygen. However it has been found that the best results are found with a feed rate of 3 ppm of DEHA for every 1 ppm of oxygen.

Catalyzed Diethyl Hydroxyl Amine - DEHA

$$C_2H_5.C_2H_5.NOH + (O) = 2CH_3.COOH + 2N_2 + H_2O$$

1. DEHA does not add to TDS in boiler water.
2. Since it is volatile it reacts with O2 in steam and condensate system.
3. Acts as a passivating agent& converts Fe2O3 to Fe3O4.
4. DEHA does not break down and therefore does not affect copper.

N,N-DIETHYLHYDROXYLAMINE ($(CH_3CH_2)_2NOH$) – DEHA

In the boiler , the DEHA reaction also forms acetic acid to some degree. This is neutralized to acetate in the boiler and eventually breaks down into carbon dioxide.

This must be taken into account when reviewing the neutralizing amine program. Decomposition of the DEHA into ammonia takes place.

However this does not occur until 534^{o}F / 279^{o}C as compared to the hydrazine break down to ammonia, which starts at 334^{o}F / 168^{o}C

N,N-DIETHYLHYDROXYLAMINE (($CH_3CH_2)_2NOH$) – DEHA

DEHA is a strong reducing agent that is capable of reverting reddish ferric oxide into magnetite in the boiler. Concentrations of 150 – 300 ppb have proven to be effective to protect boiler metal surfaces from corrosion.

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Hydroquinone ($C_6H_4(OH)_2$) HQ

Hydroquinone is usually used as a catalyst for hydrazine, DEHA, and Carbohydrazide. It is capable of acting as a stand alone oxygen scavenger.

Hydroquinone has very rapid reaction rate, even in relatively cold water. This ability enhances the performance of the products that it is used as a catalyst in and allows it to perform in low-pressure systems.

Hydroquinone (C6H4(OH)2) HQ

Hydroquinone is stable up to 572ºF / 300°C where it begins to breakdown. The final decomposition of this material is into carbon dioxide. Hydroquinone is fed at a rate of 6.9 ppm of Hydroquinone to 1 ppm of oxygen.

METHYLETHYLKETOXIME (CH3CNOCHCH3) – MEKO

MEKO is a volatile oxygen scavenger, which has a higher distribution ratio than DEHA. This allows it to operate more effectively in long run condensate systems than DEHA. The distribution ratio for MEKO is between DEAE and Cyclohexylamine.

METHYLETHYLKETOXIME (CH3CNOCHCH3) – MEKO

MEKO has the fastest reaction time of any sodium sulfite substitute. It is fed neat from a 100% solution to the feed water system at a rate of 5.4 ppm of MEKO for every 1 ppm of oxygen. The control of the is then 0.8 – 1.2 ppm in the system using an iron reduction test. MEKO does not have passivation capabilities as DEHA, so it is not recommended use in lay up.

ERYTHORBIC ACID (ERYTHROBATE) ($C_6H_8O_6$) – EA

EA is an organic acid, which is an isomer of Vitamin C. This gives the product a GRAS status for applications where the boiler water may come into contact with food production.

ERYTHORBIC ACID (ERYTHROBATE) ($C_6H_8O_6$) – EA

The pH of a 10% solution of EA is 2.1. The product is then buffered up to a pH of 5.5 with either neutralizing amines or ammonia.

ERYTHORBIC ACID (ERYTHROBATE) ($C6H8O6$) – EA

EA is catalyzed with transition metals as sodium sulfite, however if you have 1 ppb of iron in the feed water, it will be sufficient to act as the catalyst. Copper is the most effective catalyst and is added at a rate of 1 ppm of copper sulfate for every 50 parts of sodium erythorbate.

The feed rate of 10% EA is 11 ppm of EA for every 1 ppm of oxygen. This is 1.1 times the feed rate of sodium sulfite.

EA is a very strong passivating agent for iron. It can assist in the formation of passive magnetite. It is believed that break down products from the EA sequester iron and then assist in the formation of magnetite on the metal surface.

Comparison of various Oxygen Scavengers

	Catalysed sulphite	Catalyzed hydrazine	Catalyzed DEHA
Reaction rate	Excellent	average	Excellent
Metal passivation	None	Excellent	Excellent
TDS effect	None	Excellent	Excellent
Volatility	None	None	Excellent
Impact of NH3	Excellent	Poor	Excellent
Non- toxicity	Excellent	None	Average

Control of pH

- Acidity and alkalinity is determined by the number of ions found in the water.
- An ion is a positively charged atom or group of atoms. If there is an excess of hydrogen ions H + (that is, positively charged hydrogen atoms), then water is said to be acid.
- If on the other hand there is an excess of the negatively charged hydroxyl ion (OH -), then an alkaline condition is said to exist.

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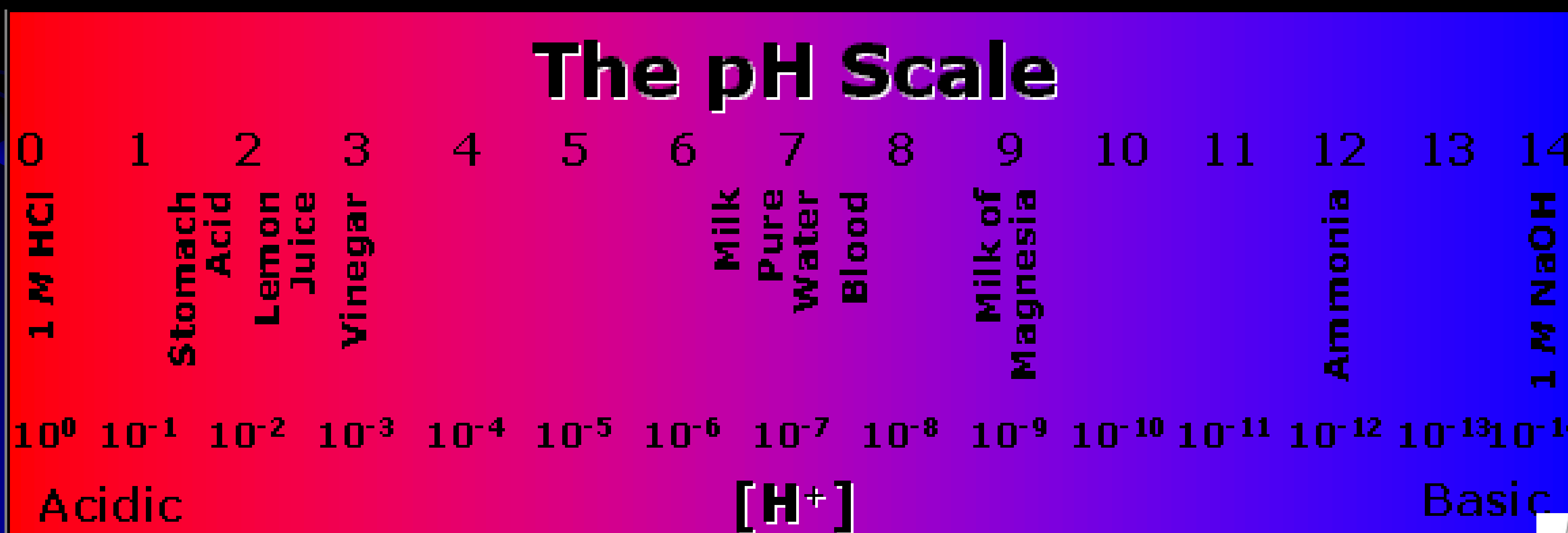
The pH scale, as used by its originator Sörensen, expresses the concentration of positively charged hydrogen ions as the "logarithm of the reciprocal of the normality of free hydrogen ions." Mathematically written this means:

$$pH = \frac{1}{\text{log 10 +H ion concentrations in gram equivalents per liter}}$$



- pH OF 0.0, THE LOWEST POINT ON THE SCALE, REPRESENTS A SOLUTION NORMAL IN HYDROGEN IONS, THAT IS TO SAY, THE STRONGEST ACID.
- pH OF 7.0 IS THE MIDDLE OR NEUTRAL POINT AT WHICH THERE IS AN EQUAL NUMBER OF HYDROXYL AND HYDROGEN IONS.
- pH OF 14-0, THE STRONGEST ALKALINE SOLUTION, MEANS THE SOLUTION IS NORMAL IN HYDROXYL IONS.

Effect of low pH

- A low pH means high concentration of H+ ions in water. This removes the metal and leads to gross corrosion.
- Depending upon the source the low pH water corrodes the pipe en route.
- The corrosion products leads to further corrosion by deposition inside boiler evaporator circuit.

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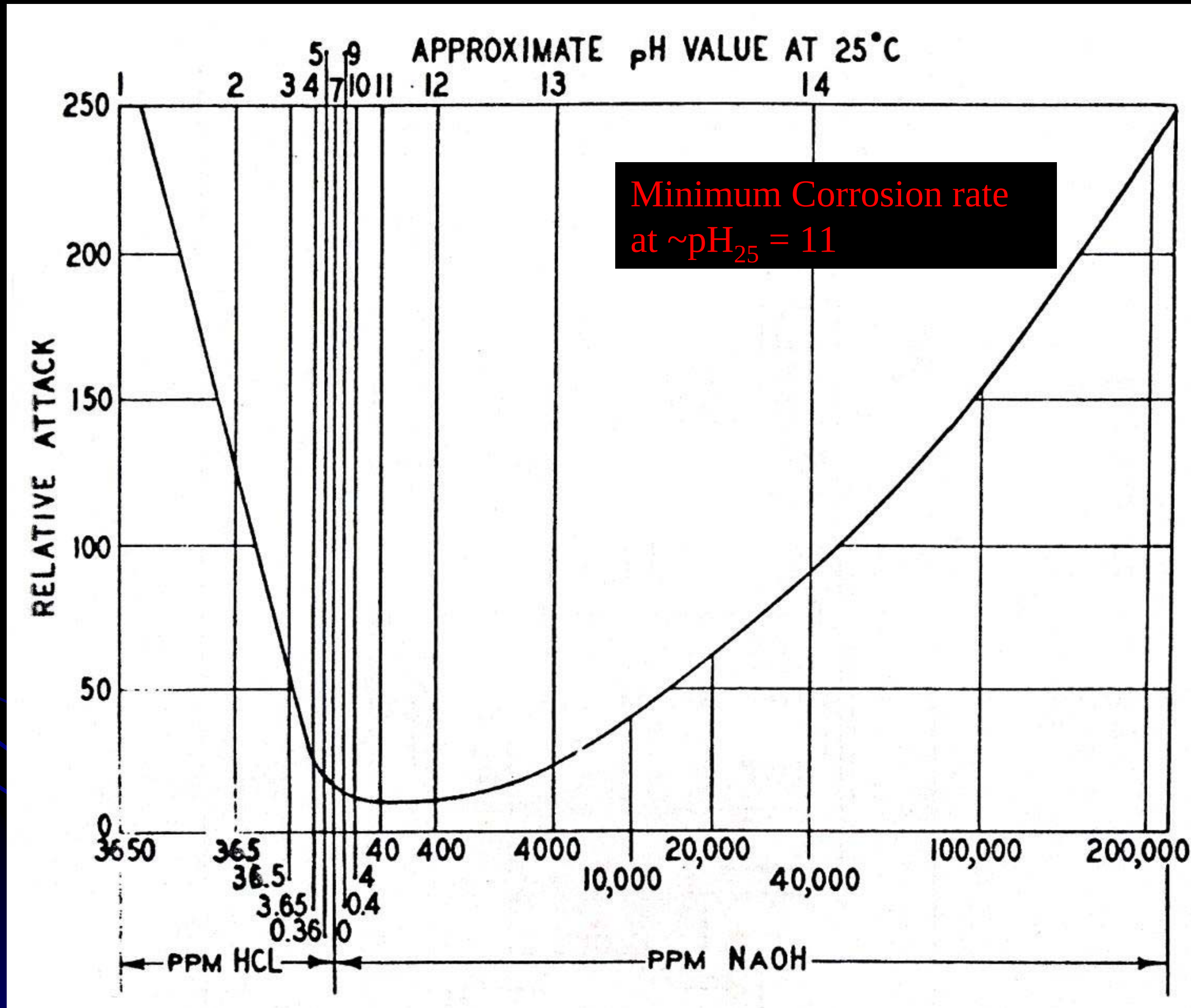

Relative Corrosion of Carbon Steel by HCl and NaOH at 310°C.

Effect of low pH

- The fine corrosion products float over the water inside steam drum and lead to foaming.
- When foaming occurs steam gets contaminated with boiler water solids and leads to deposition failure in SH coils.
- The carryover of solids also leads to turbine blade deposition. If silica is present in boiler water, the deposits will be hard to remove.

Corrosion due to low pH

- $Fe_3O_4 + HCl = FeCl_2 + H_2O + H_2$
- $Fe_2O_3 + HCl = FeCl_2 + H_2O + H_2$
- $Fe + HCl = FeCl_2 + H_2O + H_2$

Effect of low pH

- Low pH damages the boiler evaporator tubes by inter granular corrosion.
- Stressed parts get blown faster in low pH environment.

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pH boosting

- Na OH, sodium hydroxide is used to elevate the pH in feedwater.
- Morpholine / ammonia are volatile chemicals used for pH improvement in feedwater.
- Dosing should be done at the source point, such as water treatment plant or condensate storage tank.

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- Morpholine is commonly used as a pH adjustment additive in low concentrations.
- Morpholine is used because its volatility is about the same as water, so once it is added to the water in low ppm amounts, its concentration becomes distributed rather evenly in both the water and steam phases.
- Its pH adjusting qualities then become distributed throughout the steam plant to provide corrosion protection.

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- Morpholine is often used in conjunction with low concentrations of hydrazine or ammonia to provide a comprehensive all-volatile treatment chemistry for corrosion protection for the steam systems of such plants.
- Morpholine decomposes reasonably slowly in the absence of even at the high temperatures and pressures in steam systems.

Amines – pH boosters

Common Name	Boiling Point °F	Steam Distribution Ratio	Amine / Carbonate Formation	Azeotrop Formation
Cyclohexylamine	273	1.6 - 9.0	Yes	Yes
Diethylaminoethanol	325	3.1 - 4.1	No	Yes
Morpholine	262	0.3 - 0.7	Yes, Slight	No
DMA-2P	253	1.1 - 9.2	No	Yes
Ammonia	-----	10	-----	-----
Octadecylamine	450	No data	No	No

Cyclohexylamine

This neutralizing amine has generally been used for low pressure operations with long condensate returns. Pure cyclohexylamine will boil at 273°F. This corresponds to a minimum boiler pressure of 30 psig. The boiling point of the neutralizing amines are not the only criteria for evaluating their effectiveness. Cyclohexylamine goes through a mechanical function called the formation of an azeotropic mixture. The azeotropic point of a cy-clohexylamine mixture has a boiling point of 207°F. Cyclohexylamine has one of the highest steam distribution ratios. The steam distribution ratio of an amine is defined as the ratio of the amine contained in the steam vs. the amount of amine contained in the condensate at that pres-sure. This means that more cyclohexylamine will stay with the steam as pressures are reduced. Cyclohexylamine will carry out to the far reaches of the condensate system.

Cyclohexylamine has a high potential for forma-tion of an amine carbonate in condensate sys-tems. When used in steam humidification systems it is possible for odor problems to occur.

Diethylaminoethanol (DEAE)

DEAE is probably the most widely used neutraliz-ing amine today. While the boiling point of DEAE is higher than other amines (325°F) it also forms an azeoptropic mixture which is approximately 210°F. The steam distribution ratio falls midway between morpholine and cyclohexylamine. DEAE provides good general coverage to low pressure as well as higher pressure systems. DEAE does not form an amine carbonate like other neutraliz-ing amines.

Morpholine

Morpholine has one of the lowest boiling points of all amines. The boiling point of morpholine is 262°F which corresponds to about a minimum boiler pressure of 22 psig. Morpholine does not form an azeotropic mixture so a low boiling point is necessary. The steam distribution ratio for morpholine is the lowest of all amines. Mor-pholine will have more amine in the water phase than in the steam. For this reason where low pressures are involved we would not find suffi-cient amounts of amine remaining in the steam for complete coverage. Morpholine is also a very effective neutralizer up to a pH of 7.0. Its effec-tiveness drops off in trying to raise the conden-sate pH to a 8.0 to 8.5 range. Morpholine also has a slight tendency to form an amine carbonate.

Dimethylamino-2-Propanol (DMA-2P)

DMA-2P is a lesser known amine than the first three discussed. DMA-2P has a low boiling point of about 253°F. This amine also forms an azeo-tropic mixture which has a boiling point of 207°F. DMA-2P has a very high distribution ratio even higher than cyclohexylamine. DMA-2P will protect the far reaches of long distance low pressure sys-tems. DMA-2P will not form an amine carbonate in the condensate return system.

Ammonia

Ammonium hydroxide is used as a neutralizing amine in situations where live steam contacts a food product. This type of amine is the only product acceptable in dairy plant systems. Am-monia has a very high distribution ratio even higher than cyclohexylamine and DMA-2-P. Am-monia should not be fed into the feedwater or D.A. tank because of loss through the tanks vent. Ammonia is also very corrosive to copper and copper alloys.

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Ethoxylated Soya Amine

Ethoxylated soya amine is another type of film forming amine. The major difference between ODA and this type amine is that ODA has one hydrophilic attachment where the soya amine has three. This increases the solubility of the molecule resulting in a lower sludging tendency. The soya amine is therefore easier to apply and maintain. Again extreme care and monitoring are required when using this amine.

Neutralizing Capacity
ppm of amine required to raise pH to 7.5 when containing 32 ppm CO_2 at ambient temperature.

Morpholine	**84**
Cyclohexylamine	**64**
DMA-2P	**59**
DEAE	**71**
Ammonia	**14**

Phosphate – pH control- boiler water

- Phosphate-based boiler-water alkalinity control brought a major improvement to the development of programs with pH control based upon free NaOH.
- The application of phosphate either by itself, or in conjunction with caustic soda, could provide the elevated pH necessary to minimize the corrosion of carbon steel

- **Coordinated Phosphate Treatment** or captive alkalinity program was introduced by Purcell and Whirl (1943).
- It gave a significant improvement on the control of free hydroxide by placing an upper limit upon the pH (or alkalinity) allowed relative to the concentration of phosphate present.
- Coordinated phosphate treatment was simple process to monitor and control.
- To prevent the formation of free NaOH, the operator had to keep below the upper line in the plot of pH *vs.* phosphate concentration plot shown in figure. That line corresponds to three sodiums for each phosphate, *i.e*., the Na/PO4 ratio of 3.0 found in pure trisodium phosphate.

COORDINATED PHOSPHATE CONTROL

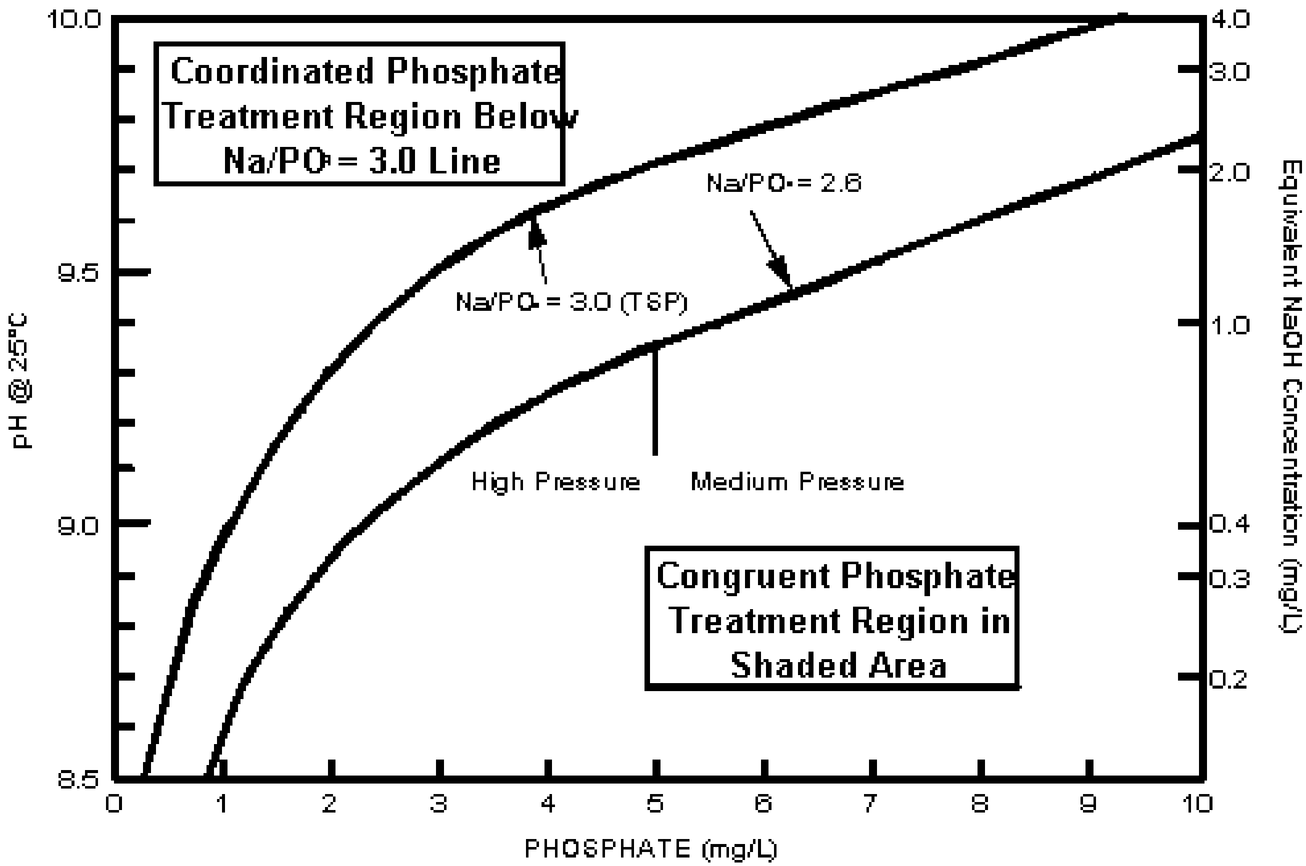

Fig. 1 - Relationship Between pH and Phosphate in Boiler Water Showing Coordinated and Congruent Phosphate Treatment Regions

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CONGRUENT PHOSPHATE CONTROL

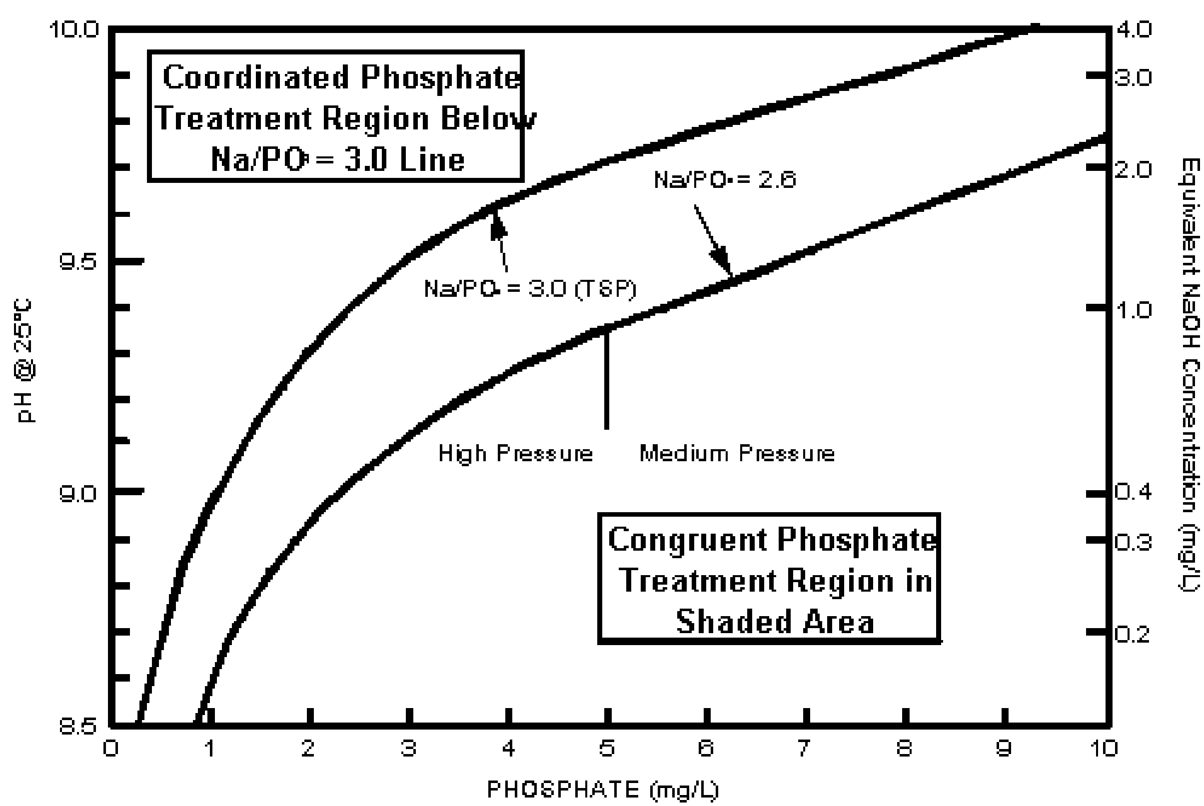


Fig. 1 - Relationship Between pH and Phosphate in Boiler Water Showing Coordinated and Congruent Phosphate Treatment Regions

Marcy and Halstead (1964) further reduced the risk of free NaOH with **Congruent Phosphate Treatment (CPT)**. This modification controlled the Na/PO4 ratio below 2.6 while also maintaining the alkalinity high enough to minimize corrosion of carbon steel.

FEED WATER SPECIFICATION :

Drum Operating pressure bar (g)	Up to 20	21 -40	41 - 60	61-100	101 & Above	Remarks
Hardness, max ppm	1.0	0.5	Nil	Nil		Note 4
pH at 25 deg C	8.8 to 9.2	8.8 to 9.2	8.8 to 9.2	8.8 to 9.2	8.8 to 9.2	Note 1
Oxygen, max ppm	0.02	0.02	0.02	0.007	0.007	
Total Iron, max ppm	0.05	0.02	0.02	0.01	0.01	
Total Copper, max ppm	0.01	0.01	0.01	0.01	0.005	
SiO_2, max ppm	1.0	0.3	0.3	0.02	0.02	Note 4
Conductivity at 25 deg C after cation exchanger in H^+ form and after CO_2 removal max μs / cm	10.0	5.0	2.0	0.5	0.3	Note 4
Hydrazine residual ppm	-	-	0.02 to 0.04	0.01 to 0.02	0.01 to 0.02	

BOILER WATER SPECIFICATION :

Drum operating pressure bar (g)	Up to 20	21 -40	41- 60	61 to 100	101 & Above	Remarks
PH at 25 deg C	10 – 10.5	10 – 10.5	9.8 – 10.2	9.8 to 10.2	9.4 to 9.7	
Phosphate residual, ppm	20 -40	20 -40	15 -25	15-25	5-10	Note 7
TDS, max ppm	500	200	150	Not more than 100	Not more than 50	Note 5
Specific electrical conductivity at 25 deg C, max μs / cm	1000	400	300	Not more than 200	Not more than 100	
Silica, max ppm	25.0	15.0	10.0	To be controlled on the basis of silica in boiler water and drum Pr. And boiler water pH relationship to maintain less than 0.02 ppm in steam leaving the drum		
Sodium sulphite as Na2SO3, ppm	20 -40	5 - 10	-			Note 2

INPUTS

Steam generation rate Nett	=	90000	kg / hr
Drum internal efficiency	=	99.5	%
Feedwater silica	=	0.03	ppm
Boiler water silica	=	2.38095	ppm
Volatile carrover %r	=	0.4	%
Drum operating pressure	=	90	kg/cm2

CARRY OVER CALCULATIONS

Drum Internal efficiency	=	99.5 %	
Percent mechanical carryover	=	100 - 99.5 %	
	=	0.5 %	
Mechanical carryover	=	2.381 x 0.5/100 ppm	
	=	0.011905 ppm	
Drum operating pressure	=	90 x 14.23 psi	
Distribution ratio %	=	0.34	
Actual vaporous carryover	=	2.381 x 100 x 0.34	
	=	0.0080954 ppm	
Total carryover of silica in steam	=	0.011905 + 0.0080954	
	=	0.0200	*Apply goal seek for reqd silica @ G19*
% blow down	=	0.03 * 100 / (2.381 - 0.03)	
	=	1.276	

OUTPUT:

Total silica carryover in steam	=	**0.02 ppm**
% blow down	=	**1.28**

INPUTS

Steam generation rate Nett =	90000	kg / hr
TDS in feed water =	0.1	ppm
TDS permitted in boiler water =	25	ppm
Oxygen in feed water =	0.02	ppm
Oxygen permitted in feed water =	0.002	ppm
Residual phosphate level in boiler water =	4	ppm
Concentration of phosphate solution =	0.3	gm / 100 ml
Residual sulphite in feed water =	15	ppm
Concentration of sulphite solution =	0.04	gm / 100 ml
Residual Hydrazine in Feed water =	0.02	ppm
Concentration of hydrazine solution =	35	%

HP CHEMICAL DOSING CALCULATION

Chemical Dosed in HP Dosing System	=	**TRI SODIUM PHOSPHATE**
Maximum steam generation capacity of boiler	=	90000 kg /hr
TDS in feedwater	=	0.1ppm
TDS permitted in Boiler water	=	25 ppm
Percentage blow down	=	100 x 0.1 / (25-0.1)
	=	0.4 %
Actual blow down rate	=	90000 x 0.4/100 kg/ hr
	=	360 kg/hr
Recommended phosphate ppm in boiler water	=	4 ppm
Loss of phosphate in blow down water	=	4 x 360 / 1000 g / hr
	=	1.44 gm / hr
Loss of TSP in blow down water	=	1.44 x 4
	=	5.76 gm/h
Tri sodium phosphate consumption per day	=	5.76 x 24 / 1000 kg / day
	=	**0.13824 kg / day**

OUTPUT:

Tri Sodium Phosphate Consumption per day = 0.13824 Kg / Day

LP CHEMICAL DOSING CALCULATION

Chemical dosed	=	**HYDRAZINE**
Maximum steam generation capacity of boiler	=	90000 kg / hr
Oxygen in feedwater	=	0.02 ppm
Required oxygen level in feed water	=	0.002 ppm
Oxygen to be removed	=	0.02 - 0.002 ppm
	=	0.018 ppm
Hydrazine required (thirty times)	=	30 x 0.018 ppm
	=	0.54 ppm
Residual hydrazine to be kept	=	0.02ppm
Total hydrazine required	=	0.54 + 0.02 ppm
	=	0.56 ppm
Total hydrazine required in kg/kg of evaporation	=	0.56 x 0.000001 kg / kg
	=	0.00000056 kg / kg
Hydrazine required per hour	=	90000 x 0.00000056 kg / hr
	=	0.0504 kg / hr
Concentration of hydrazine solution	=	35%
Hydrazine to be dosed @35% conc	=	0.0504x100 / 60kg / hr
	=	0.144kg / hr
Hydrazine consumption per day	=	0.14400x 24 kg / day
	=	**3.456 kg / day**

3-2.7.2 **Estimating Carbon Dioxide in Steam**. Corrosion engineers find it useful to know the amount of carbon dioxide (CO_2) in steam when assessing the return on investment (i.e., cost savings from removing the CO_2 versus the cost for use of internal chemical treatment to remove the CO_2). Engineers and water treatment service companies need to estimate the amount of CO_2 to properly estimate the amount of neutralizing amine water treatment chemical that must be used. Example 3-5 illustrates this estimation:

CO2 levels in the steam can be estimated from the amount of bicarbonate and the carbonate alkalinity present in the feedwater as follows, where the "P" and "M" alkalinity measure these compounds. (See paragraph 6-6.1 for test methods.)

EQUATION

$$CO_2 = [\text{bicarbonate} \times 0.79] + [\text{carbonate} \times 0.35] \quad (18)$$

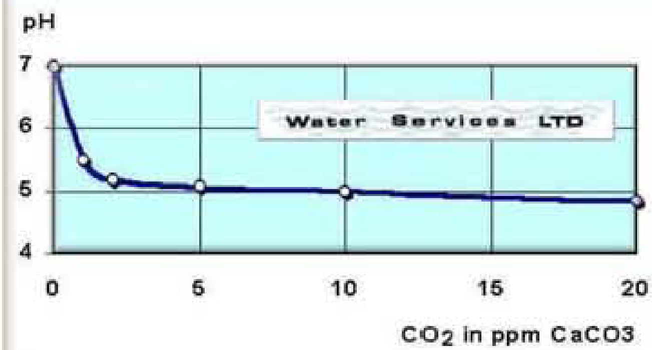
$$CO_2 = [(M - 2P) \times 0.79] + [2P \times 0.35]$$

where:

CO_2 = carbon dioxide estimate, ppm as CO_2
M = total (methyl orange) alkalinity, ppm as $CaCO_3$
P = phenolphthalein alkalinity, ppm as $CaCO_3$

Table 3-4. Physical and Chemical Properties of Neutralizing Amines

Property	Morpholine	DEAE	Cyclohexylamine
Boiling point (100% amine)	129 °C (264 °F)	163 °C (325 °F)	134 °C (273 °F)
Boiling point (amines/water azeotrope)	--	99 °C (210 °F)	96 °C (205 °F)
Decomposition temperature	340 °C (644 °F)	423 °C (794 °F)	330 °C (626 °F)
Vapor-liquid distribution ratio	0.4	1.7	4.7
Specific gravity (100% amine)	1.002	0.88	0.86
pH, 100 ppm solution	9.7	10.3	10.7
Amount of amine required to maintain pH of 8.0 in water containing 10 ppm CO_2	37 ppm	22 ppm	15 ppm



pH for a 10 ppm of CO2 as per graph = 5 (pH may be higher after start up)

Amine required as per table above to improve pH to 8 = 37

Boiler steam generation rate = 90000 LPH

therefore chemical dosage rate, kg/h = 90000 x 37 / 10^6

= 3.33

% dilution by water = 5

(dilution to be adjusted to match pump capcity)

Actual dosage rate, LPH = 16.65

Pump capacity selected = **20 LPH**

OUTPUT:

Sodium Sulphite comsumption per day = 0.3062 Kg / Day

Hydrazine Consumption per Day = 3.456 Kg / Day

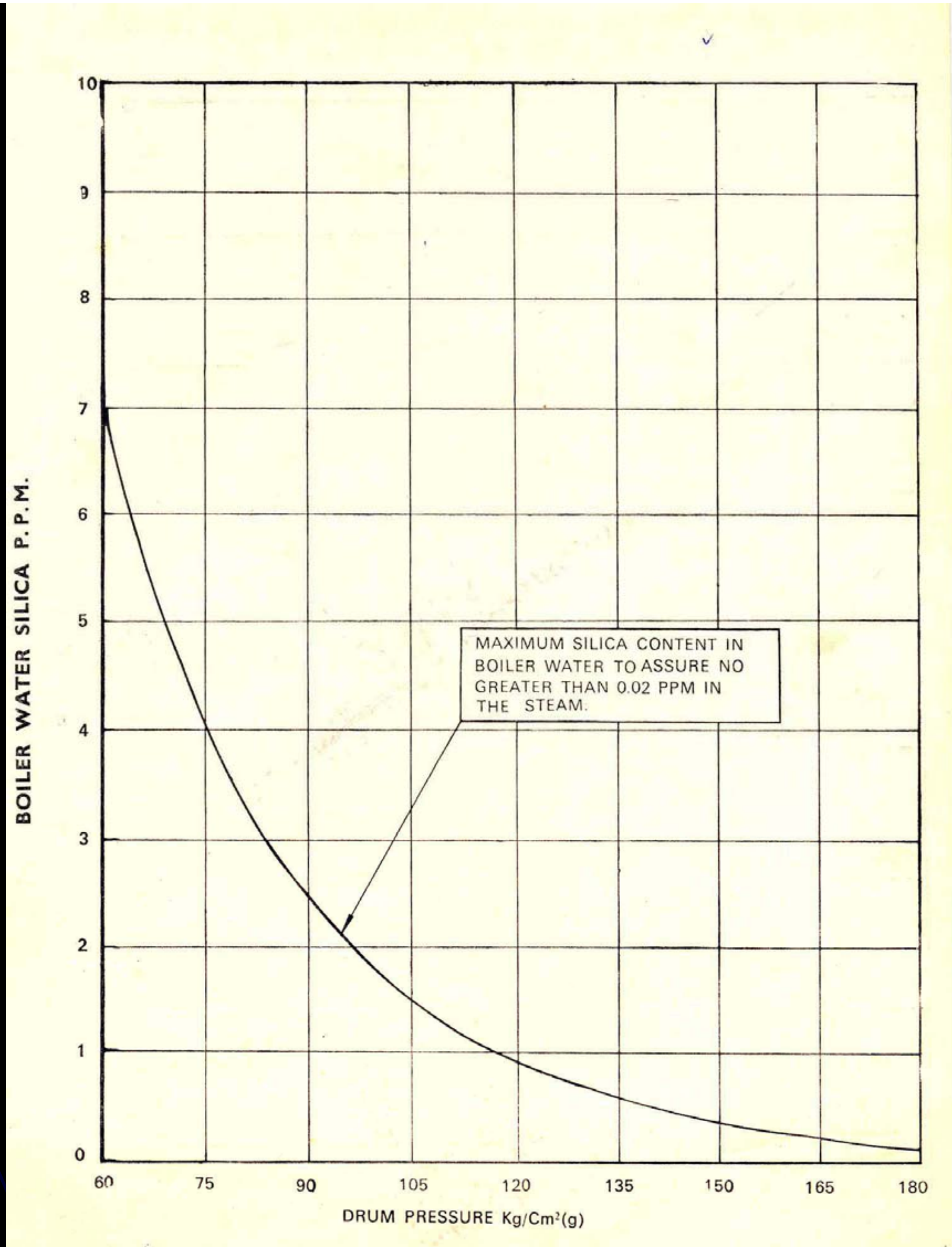
Morpholine Consumption per Day (max) = 79.92 Kg / Day

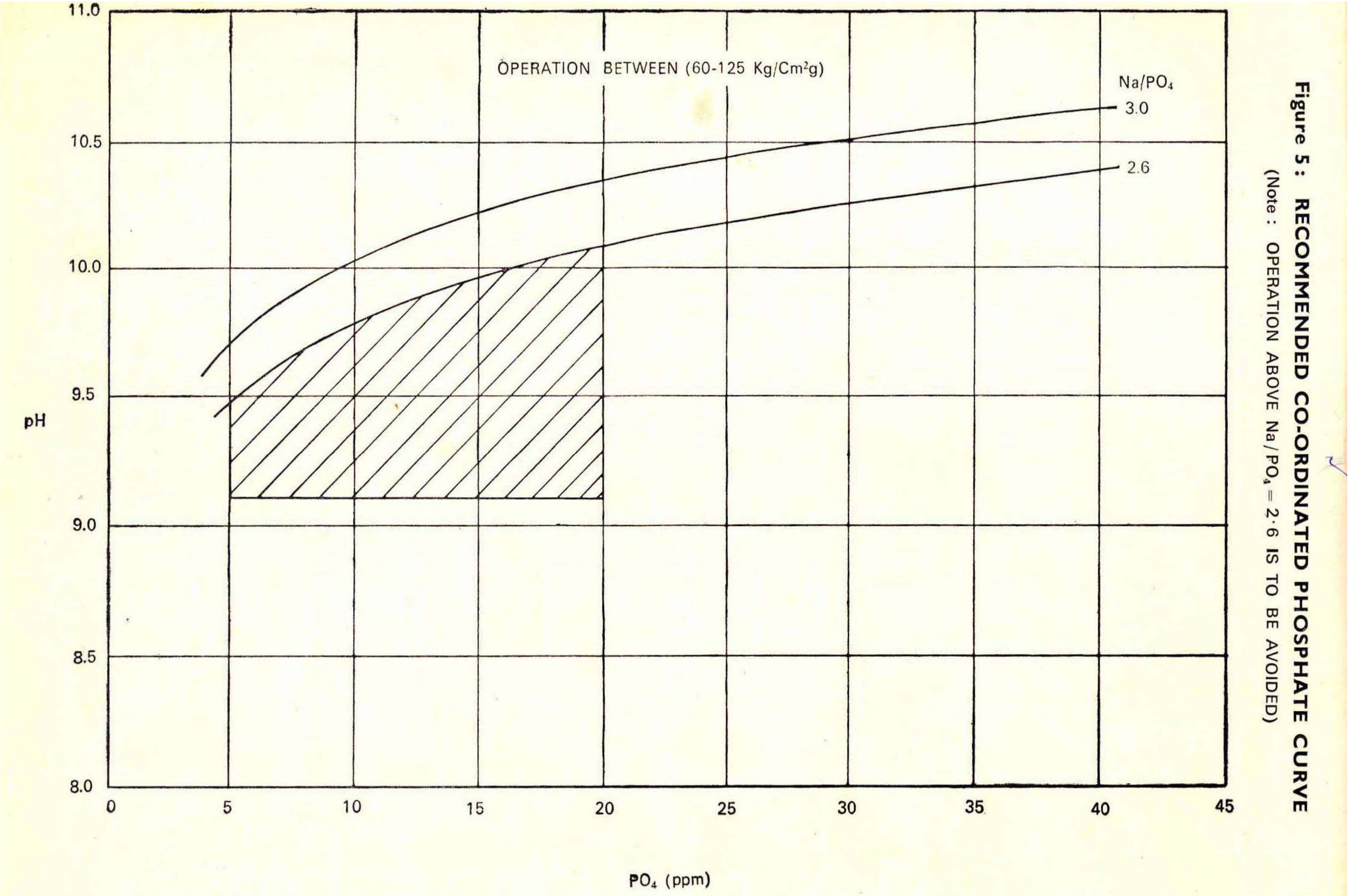
Table 3-5. Neutralizing Amine Selection Chart

Amine	Low Pressure (below 103 KPa [15 psig])	High-Pressure Systems (above 103 KPa [15 psig])		
		Short System < 243 m (< 800 ft)[2]	Medium System < 1.61 km (< 1 mile)[2]	Long System > 1.61 km (> 1 mile)[2]
Morpholine		X		
DEAE	X		X	X
Cyclohexylamine [1]	X			
Cyclohexylamine/ morpholine mixture			X	X

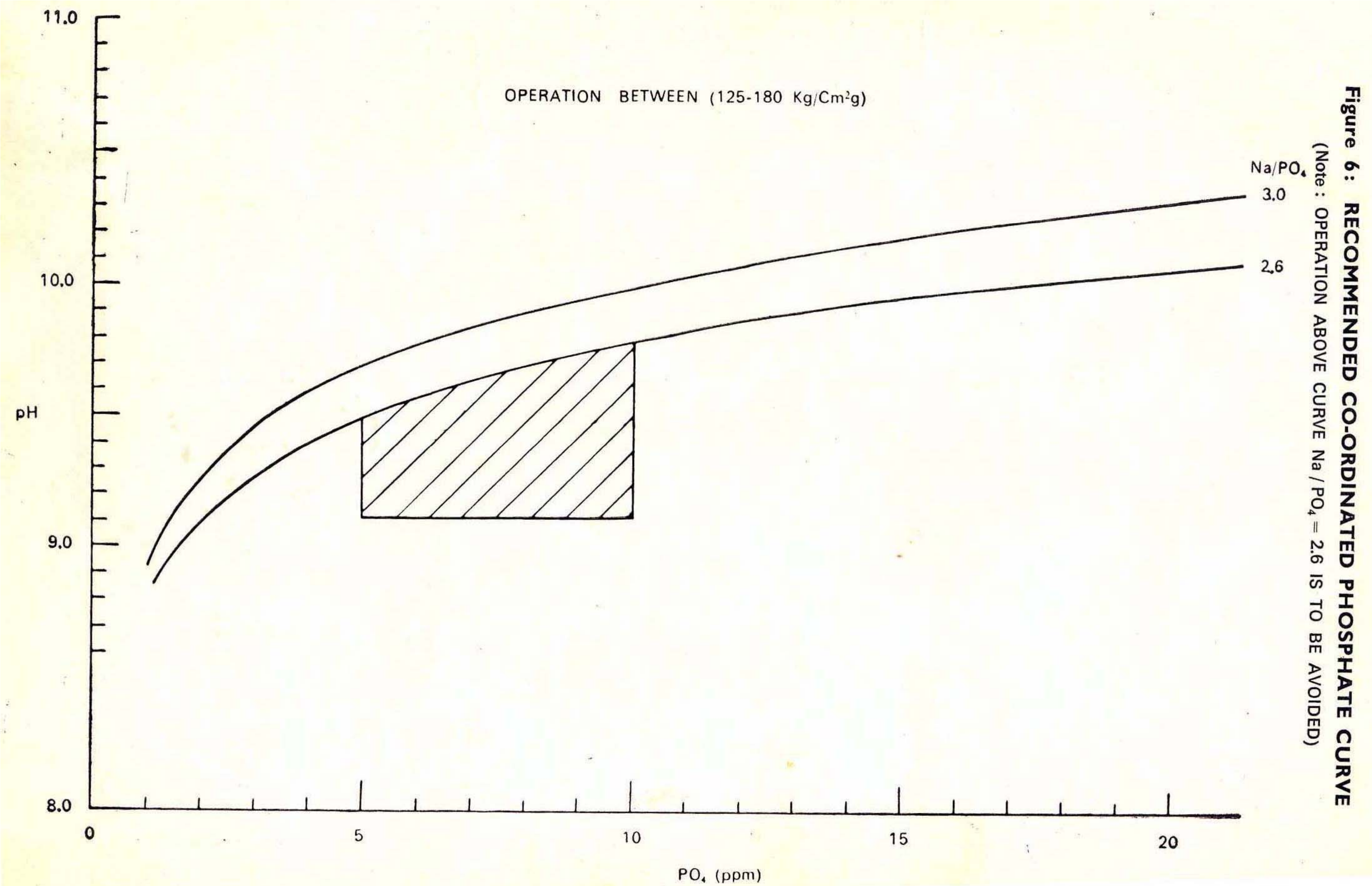
Tube failures

As the drum pressure goes up silica has to be restricted to limit silica carryover

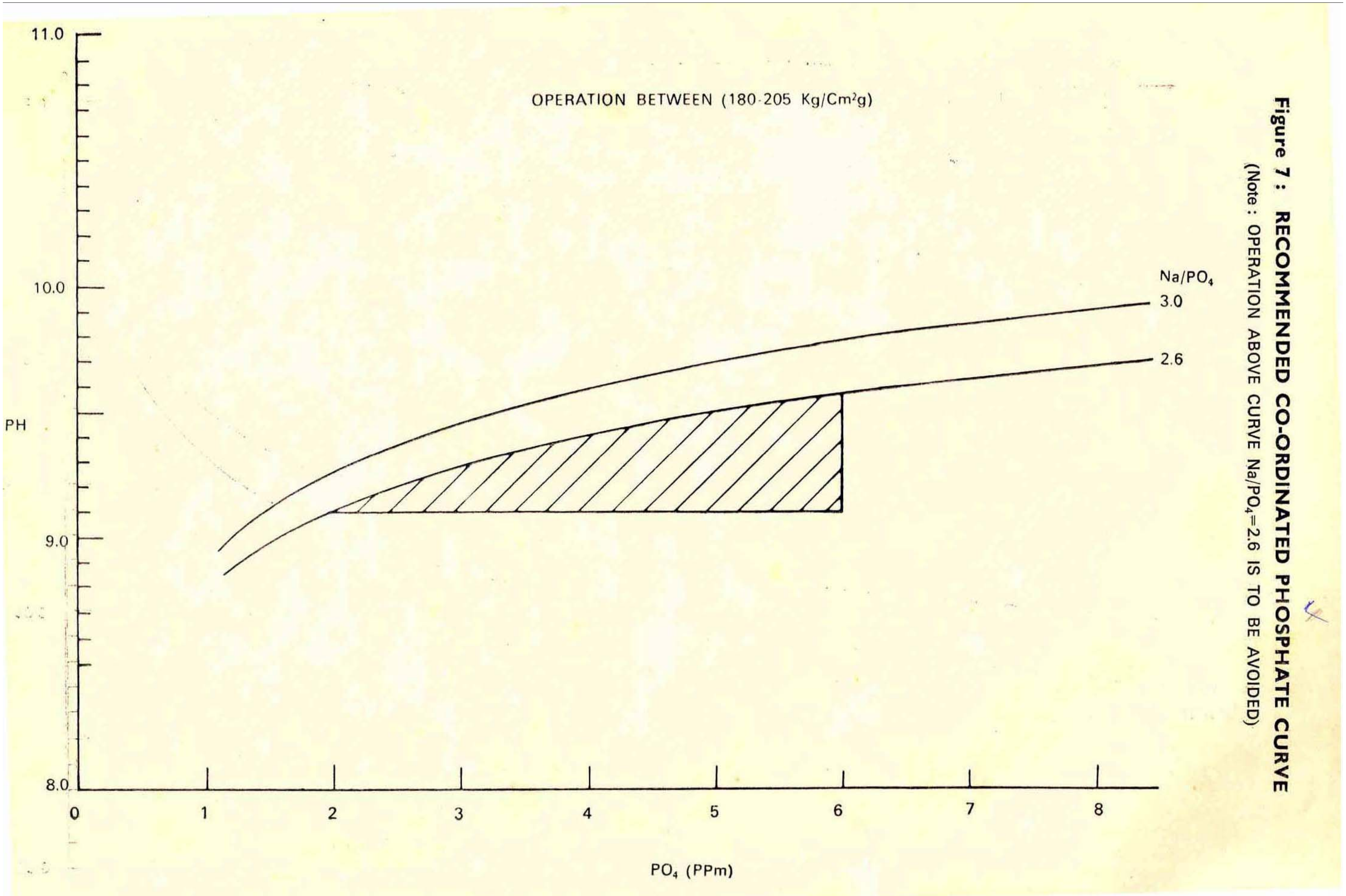




Coordinated pH - PO4 curve



Coordinated pH - PO4 curve



Coordinated pH - PO4 curve

- Overheating
- Corrosion
- Caustic gouging
- Hydrogen damage
- Thermal fatigue
- Flow assisted corrosion

Corrosion damage at ECO

OVERHEATING

Overheating is exceeding the safe metal temperature beyond which the metal is unable to withstand the service pressure

OVERHEATING

Overheating is classified into short term and long term overheating.

SHORT TERM OVERHEATING

Short-term overheating frequently exhibits a thin-lipped longitudinal rupture, accompanied by noticeable tube bulging, which creates the large fish-mouth appearance as shown .

Short-term failure can be caused

- by low water level
- partial or complete pluggage of tubes
- rapid start-ups
- excessive load swings
- excessive heat input

Rapid overheating – circulation defect

----Virtually all tubes, which carry water or steam and are exposed to high operating temperatures are susceptible to this type of failure.

----The more violent ruptures occur at tube metal operating temperatures well above the oxidation limits of the material and typically above the eutectoid transformation temperature of 1340°F (727°C).

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Peak metal operating temperatures above the eutectoid can be estimated by the amount of bainite or martensite mixed with ferrite in the metal microstructure at the failure origin

LONG TERM OVERHEATING

-OCCURS IN SUPERHEATER, REHEATER, EVAPORATOR SECTIONS.

AS A RESULT OF GRADUAL ACCUMULATION OF DEPOSITS OR SCALE, PARTIALLY RESTRICTED STEAM OR WATER FLOW, EXCESSIVE HEAT INPUT FROM BURNERS OR UNDESIRED CHANNELING OF FIRESIDE GASES.

LONG TERM OVERHEATING

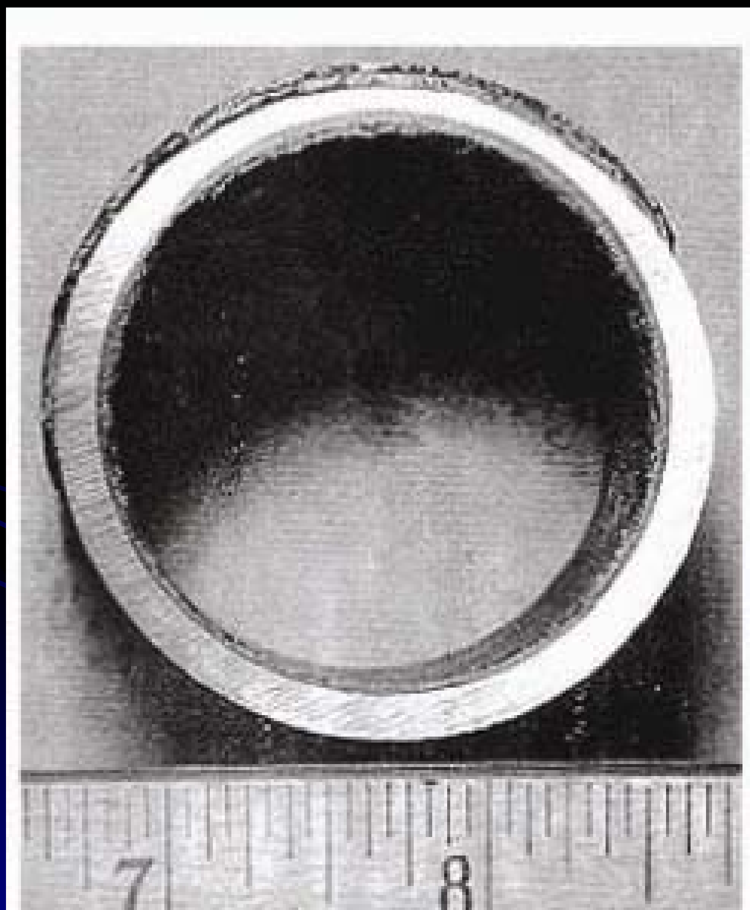
Horizontal or inclined tubes subjected to steam blanketing are also prone to long-term overheating failures. Bed coils of AFBC boiler suffer from this failure due to scale / circulation defect.

Tube metal operating temperatures above 850°F (454°C), or slightly above the oxidation limits of the tube steels, can lead to blistering, tube bulging or thick-lipped creep rupture failures.

SWELLING AND BLISTERING OF TUBES DUE TO LONG TERM OVERHEATING

Suspended solids carryover to SH

OXIDATION OF SUPERHEATER TUBE – INTERNAL AND EXTERNAL OXIDATION



LONG TERM OVERHEATING

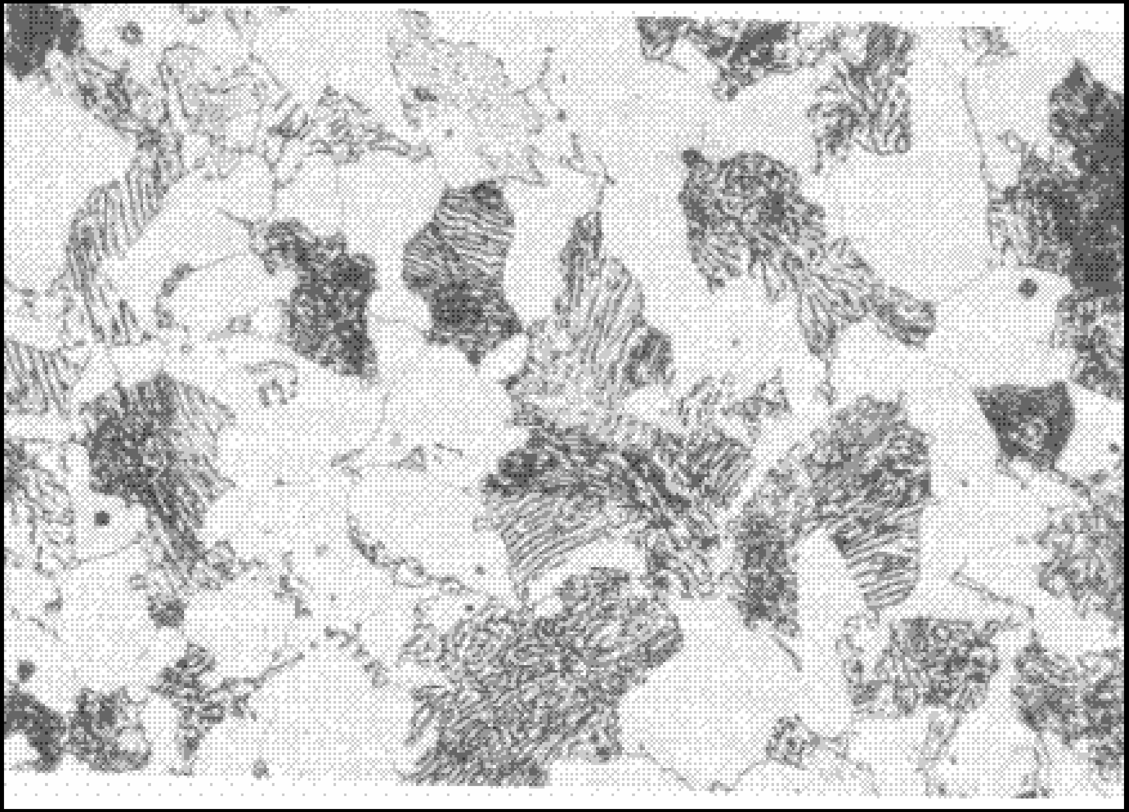
A Long term overheating failures can not be predicted easily by visual means. Over a period there is a gradual change in microstructure leading to loss of strength and the failure occurs. The metal should be removed and inspected under microscope

LONG TERM OVERHEATING- stage 1

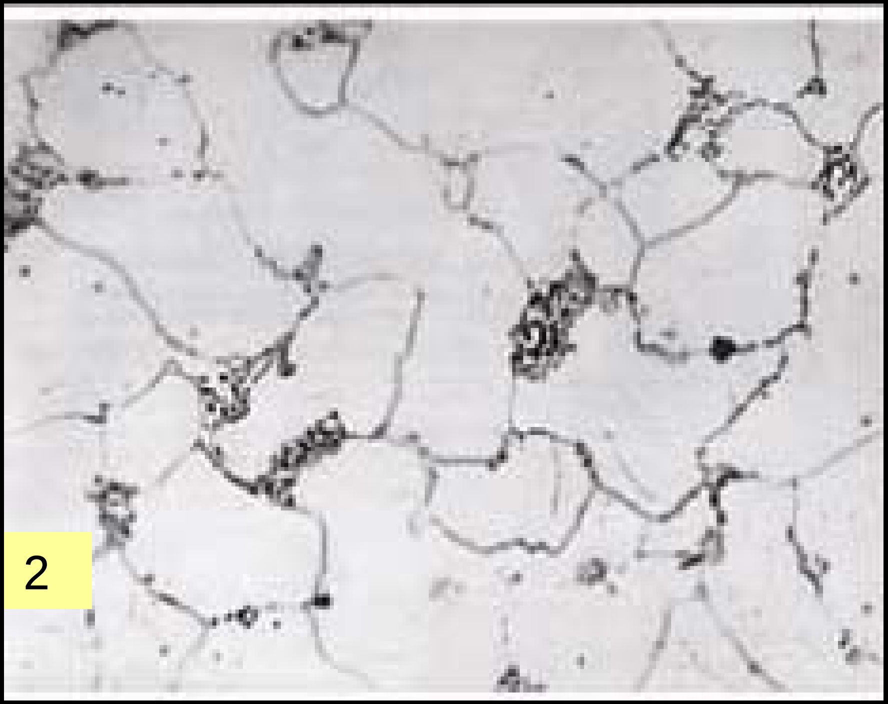
Normal steel

The white boundary
- Ferrite

The black boundary
- Pearlite



LONG TERM OVERHEATING- stages



1. Ferrite + Pearlite
2. Spheroidization of carbide

LONG TERM OVERHEATING- stages

3. Advanced stage of spheroidization
4. Completed graphitization – material loses strength

Caustic gouging

It is the concentration of alkali in boiler evaporative circuits which leads to ductile corrosion of tubes.

When & Where

- Low sloped tubes where heat input is less and circulation is also poor.
- Low sloped tubes where heat input is high and the slope is inadequate to permit mixing of steam and water.
- Occurs due to slight departure from nucleate boiling (DNB).
- The departure is not sufficient to cause overheating. Otherwise overheating failure would be immediate.
- When water chemistry is deviated and free OH is available.

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Mechanism in high heat flux tubes and low sloped tubes.

- The high steam rate leads to stratified flow.
- This happens if the inlet velocity of water at the tube is inadequate to carry the steam bubbles with water.
- if the slope of the tube is inadequate for buoyant movement of steam in to the water.
- Happens only after steaming point.

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Mechanism in low heat tubes and low sloped tubes.

- The inlet velocity is inadequate. There is no gross movement of water as per design.
- The steam bubbling rate is so less. The steam bubbles out leaving the water concentrated.
- if the slope of the tube is inadequate for buoyant movement of steam in to the water.
- Happens only after steaming point.

Inside of tube showing the caustic gouging

CAUSTIC ATTACK

Sodium hydroxide (NaOH) is used extensively in boiler water treatment to maintain the optimum hydroxyl ion concentration range to form a protective magnetite film on steel surfaces and to help form non-adherent sludges when hardness enters the boiler

CAUSTIC ATTACK

However, excessive sodium hydroxide can destroy the protective film and corrode the base metal as shown in equations 2 and 3. NaOH can concentrate during departure from nucleate boiling (DNB), film boiling or steam blanketing conditions. Concentration also occurs when normal boiler water evaporates beneath deposits leaving behind the caustic at the metal surface.

Caustic corrosion

Caustic concentration due to deposits

- Due to fouling by porous deposits such as iron oxides & copper oxides.
- Deposits are formed from particles suspended in boiler water.
- Once the corrosion mechanism is started, the corrosion products lead to chain mechanism.

Caustic concentration under deposits

- Boiler water permeates the porous deposits by capillary action through small pores like a liquid permeating a wick.
- Steam escapes through larger pores (channels) leaving non volatile solutes behind. These new deposits concentrate beneath the deposits.
- Like feedwater concentrating in boiler, the solid concentrates to 2000 times beneath porous deposits.

Caustic concentration under deposits

- Once the local caustic concentrations are reached the tube metals fails by irregular thinning of tube wall.
- The microstructure does not change at the failure point. The tube retains ductility.
- Boiler water solids are present at the failure locations.
- Another form of failure is hydrogen damage which can occur at pressures above 1000 psig.

Caustic damage

Caustic attack below deposits

Caustic gouging attacks due to DNB

Caustic corrosion mechanism

Magnetite is the co polymer of iron oxide II & Iron oxide III. That is, FeO is a solid solution in Fe2O3.

The bond of divalent iron is easily hydrolyzed. The iron hydroxide (aqueous) is considered to be in solution equilibrium with magnetite as follows

$$Fe_3O_4 + 2\ H_2O = Fe\ (OH)_2 + 2\ FeO.OH$$

Caustic corrosion mechanism

Under highly alkaline conditions, the ferrous hydroxide in solution may react as follows.

$$Fe(OH)_2 + OH- = FeOH_3 = HFeO_2^{\ -} + H_2O$$

$$Fe(OH)_2 + 2\ OH^- = Fe(OH)_4 = FeO_2^{-2} + 2.H_2O$$

In this manner, the attack occurs removing the passive layer and inhibiting its formation. A velvet black, finely crystalline, reactive magnetite is seen in the corrosion zone.

Acid Corrosion / low pH Corrosion

One mechanism for acid corrosion involves thermally induced reaction of permanent hardness salts in an operating boiler.

$$MgCl_2 + 2H_2O = Mg(OH)_2 + 2\,HCl$$

Similarly HCl can form from calcium salts.

Acid Corrosion / low pH Corrosion

- $Fe_3O_4 + HCl = FeCl_2 + H_2O + H_2$
- $Fe_2O_3 + HCl = FeCl_2 + H_2O + H_2$
- $Fe + HCl = FeCl_2 + H_2O + H_2$

Acid Corrosion / low pH Corrosion

- Condenser leakage, where hardness salts deplete the phosphate and hydroxide ions, also can cause acid corrosion.
- In the above case, hydrochloric acid / sulfuric acid can form.
- Hydrochloric acid also forms when the chloride ion finds its way underneath a deposit where hydroxide ions have been depleted by ferrous ions formed by corrosion cell.

HYDROGEN DAMAGE

- HYDROGEN WHEN PRESENT DIFFUSES THROUGH THE GRAIN BOUNDARIES AND CAUSES INTERGRANUALR CRACKS AND AT TIMES BLOWS THE METAL OUT.

HYDROGEN DAMAGE CAN OCCUR UNDER FOLLOWING CONDITIONS

- LOW pH WATER PRESENT IN STRESSED ZONE.
- HYDROGEN RELEASE BENEATH DEPOSITS.

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REACTIONS OF H2 WITH METAL

- 4H + Fe3C (pearlite) = CH4 + Fe (ferrite)

The hydrogen ions being small in atomic diameter easily travels along boundary and causes methane formation on heating. Methane expands and leads to inter-granular crack.

EXAMPLE OF HYDROGEN DAMAGE IN STRESSED PART OF BOILER TUBE

High caustic damage – Hydrogen generation

Hydrogen damage occurs in boilers operating usually above 1000 psig (6.9 MPa) and under heavy deposits or other areas where corrosion releases atomic hydrogen. Concentrated sodium hydroxide beneath the deposits can remove the protective magnetite film by the following reactions.[3]

$4NaOH + Fe_3O_4 = 2NaFeO2 + Na2FeO2 + 2H2O$ (1)

Concentrated sodium hydroxide can then react with freshly exposed base metal to yield sodium ferrate and atomic hydrogen:

Fe + 2NaOH =Na2 FeO2 + 2H (2)

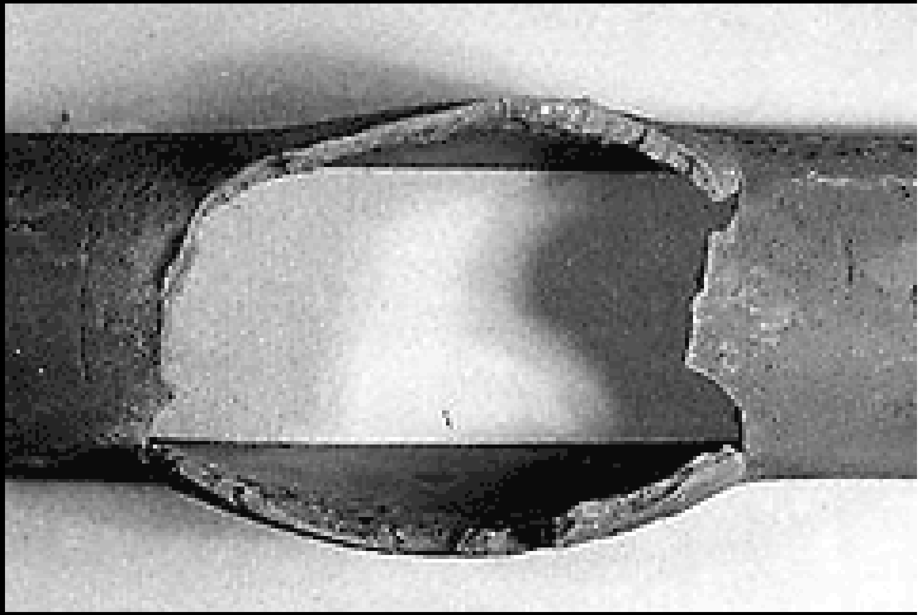
The hydrogen produced at the metal surface can diffuse into the steel where it can combine to form molecular hydrogen or react with iron carbide to form methane and iron: The failed area is thick lipped and the failure is brittle in nature.

4H + Fe3C = CH4 + 3Fe (3)

Microstructure with cracks
due to H2 diffusion

Hydrogen damage blo

Metal blown out due
to H2 diffusion



Other reasons for Hydrogen damage

- Upsets in phosphate treatment programs or residual acid from chemical cleanings can also cause hydrogen damage, especially if the acids remain trapped beneath the deposits.
- In non drainable sections, the acid trapped in chemical cleaning operation can cause this damage.

Picture at failure locations

- Failures are typically characterized as thick-lipped, brittle type ruptures.
- Sometimes, thick-walled "windows" can be completely blown out of the tube wall.
- Micro-structural examination at the area of failure typically reveals short discontinuous inter-granular cracks accompanied by decarburization as seen in photograph.

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OXYGEN DAMAGE

- The presence of dissolved oxygen in boiler water causes the cathode of any corrosion cell to depolarize, thereby sustaining the corrosion process.
- Formation of reddish brown hematite (Fe_2O_3) or "rust" deposits or tubercles accompanied by hemispherical pitting is the most familiar form of oxygen attack as shown.

Acid corrosion

Acid forms due to permanent hardness salts in an operating boiler. Magnesium salts result in reduction of boiler water pH to the range of 4 to 4.5.

$MgCl_2 + 2 H_2O = Mg(OH)_2 + 2 HCl$

Similar reactions can occur with calcium salts.

OXYGEN DAMAGE

- Oxygen pitting is frequently seen in economiser tubes where the tubes are horizontal.
- Oxygen damage is more in an idle boiler.
- Improper off line storage practices lead to more damage.

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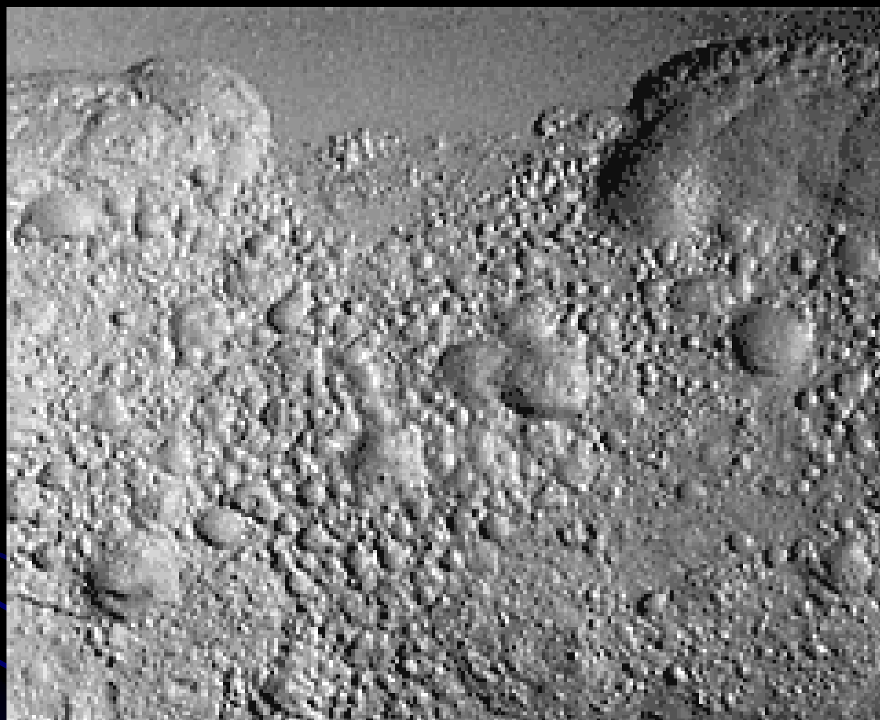

Oxygen pitting- characterized by local pits and cluster of pits around a rusted area.

THERMAL FATIGUE

- This damage results from cyclic and excessive thermal fluctuations accompanied by mechanical constraint.
- Excessive temperature gradients can add to internal strain to initiate or enhance the cracking process.
- Once initiated, freshly exposed metal within the cracks can undergo oxidation, creating a wedge effect at the crack tip, since the oxide occupies a greater volume than the base metal.

LOCATIONS FOR THERMAL FATIGUE

- THERMAL FATIGUE CAN OCCUR IN WATERWALLS FINS OR HEADERS STUBS
- OTHER AREAS SUBJECTED TO DNB
- RAPIDLY FLUCTUATING FLOWS.
- LOW-AMPLITUDE VIBRATIONS OF ENTIRE SUPERHEATERS CAN LEAD TO THERMAL FATIGUE.

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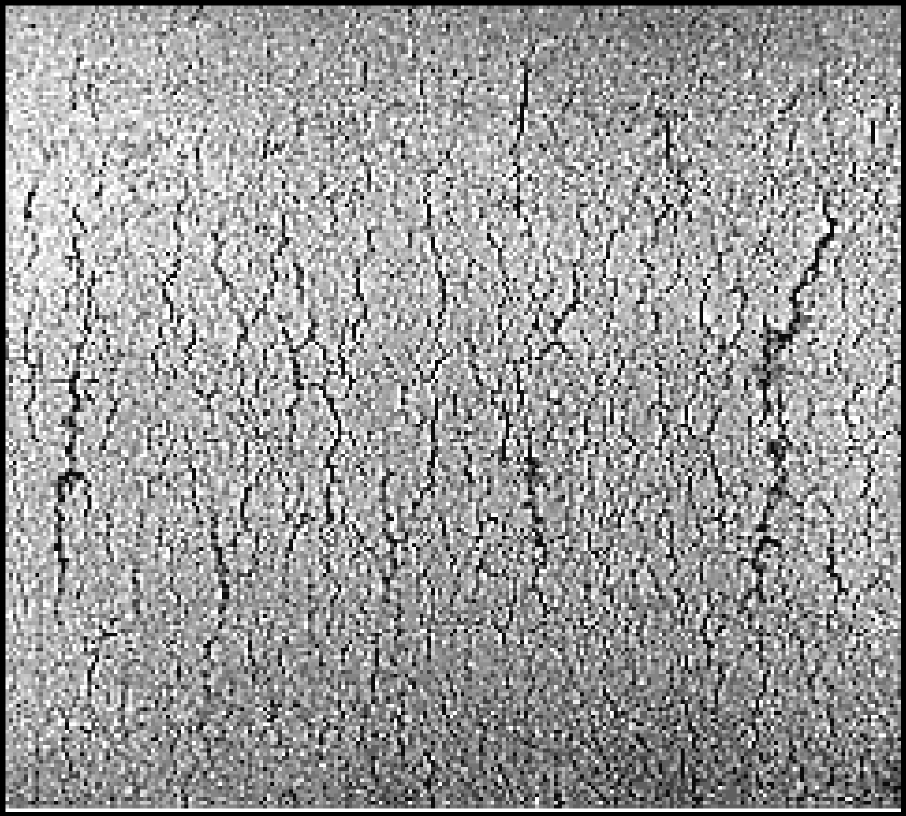
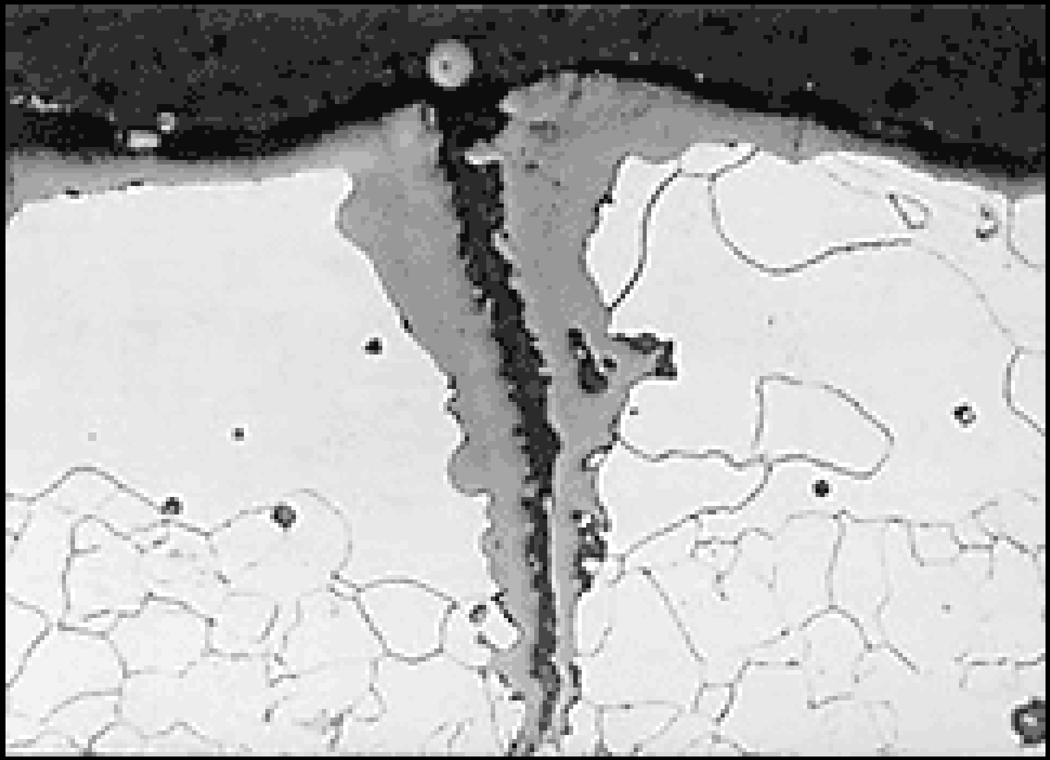
EVIDENCES OF THERMAL FATIGUE

Thermal fatigue damage typically exhibits numerous cracks and crazing



EVIDENCES OF THERMAL FATIGUE

MICROSTRCURE IN DAMAGED PORTION.



FLOW ASSISTED CORROSION

Flow assisted corrosion (FAC) is the localized thinning of a component related to the dissolution of the protective oxide film and the underlying base metal

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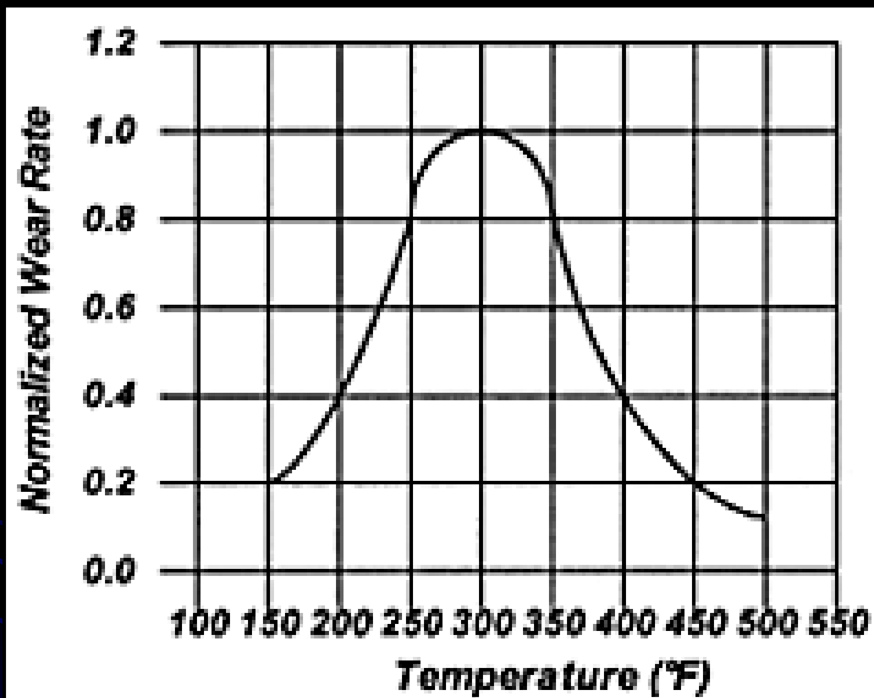
FLOW ASSISTED CORROSION

FAC is typically seen in single or two phase water flowing in carbon steel piping. The more common locations where FAC is detected are:

- Low pressure system bends in evaporators, risers and economizer tubes
- Feed water system (due to more volatile chemistry and lower pH)

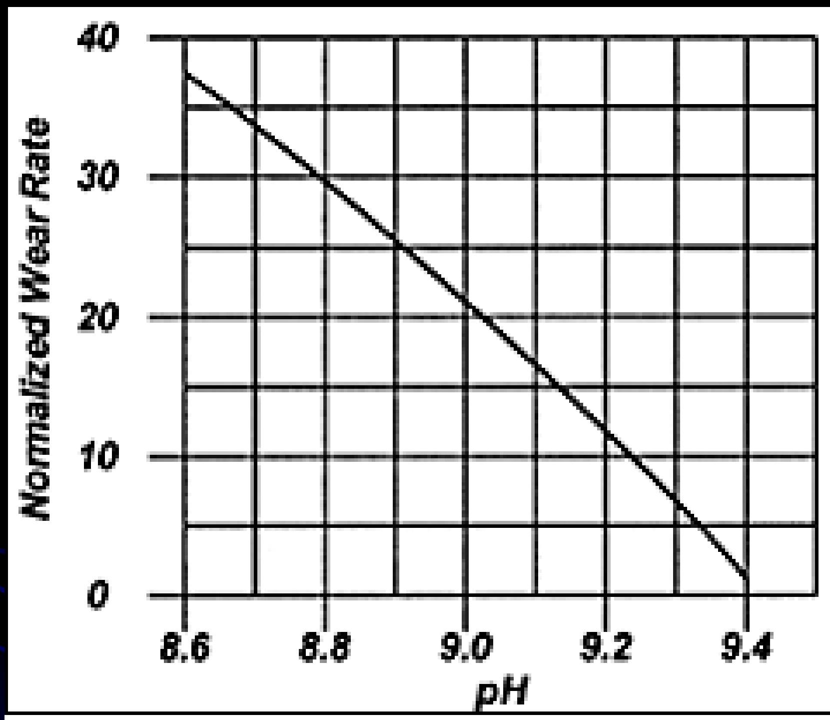
- Temperature
- pH
- Oxygen concentration
- Mass flow rate
- Geometry
- Quality of fluid (single or two phase)
- Materials of construction

Effect of temperature on FAC



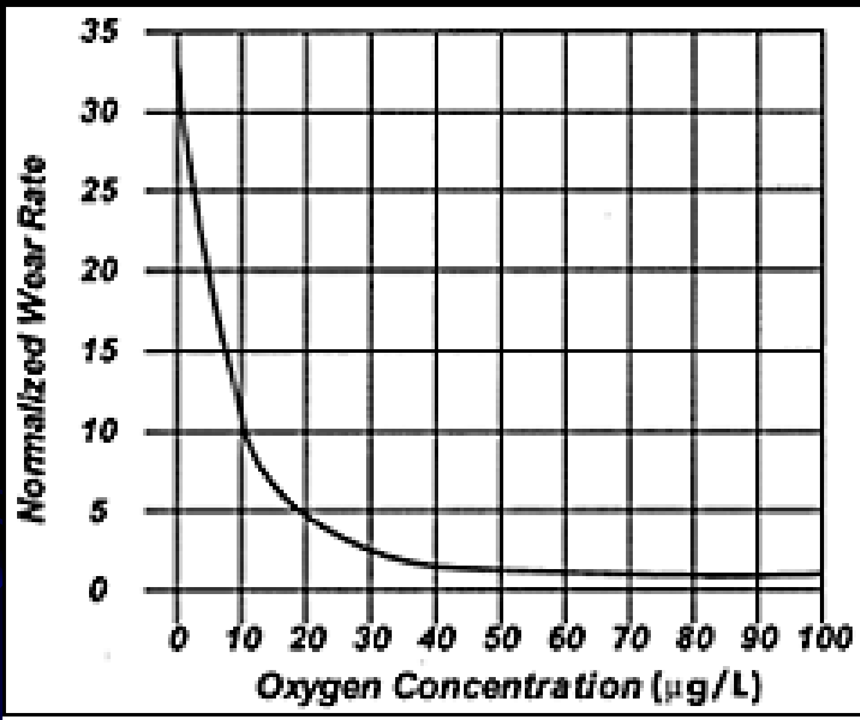
The greatest potential for normalized wear occurs at around 300°F (149°C), with very little potential for FAC below 150°F (66°C) and above 500°F (260°C).

Effect of pH on FAC



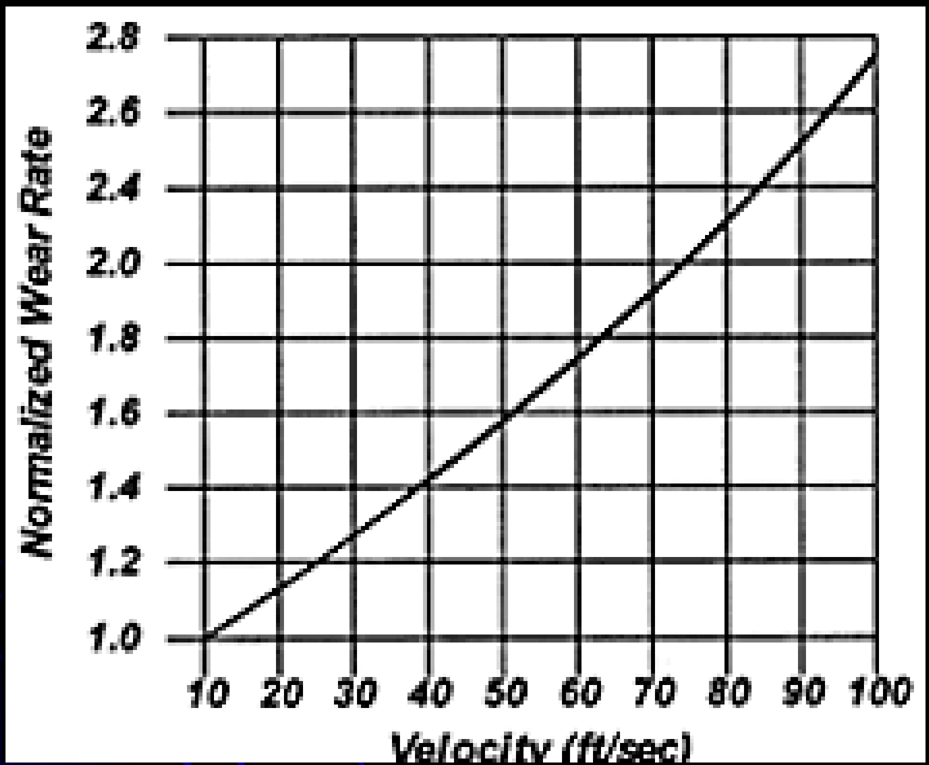
As with general corrosion, pH has a significant effect on the normalized wear rate of carbon steel. There is almost a forty (40) fold reduction in wear rate between a pH of 8.6 and a pH of 9.4

Effect of dissolved oxygen on FAC



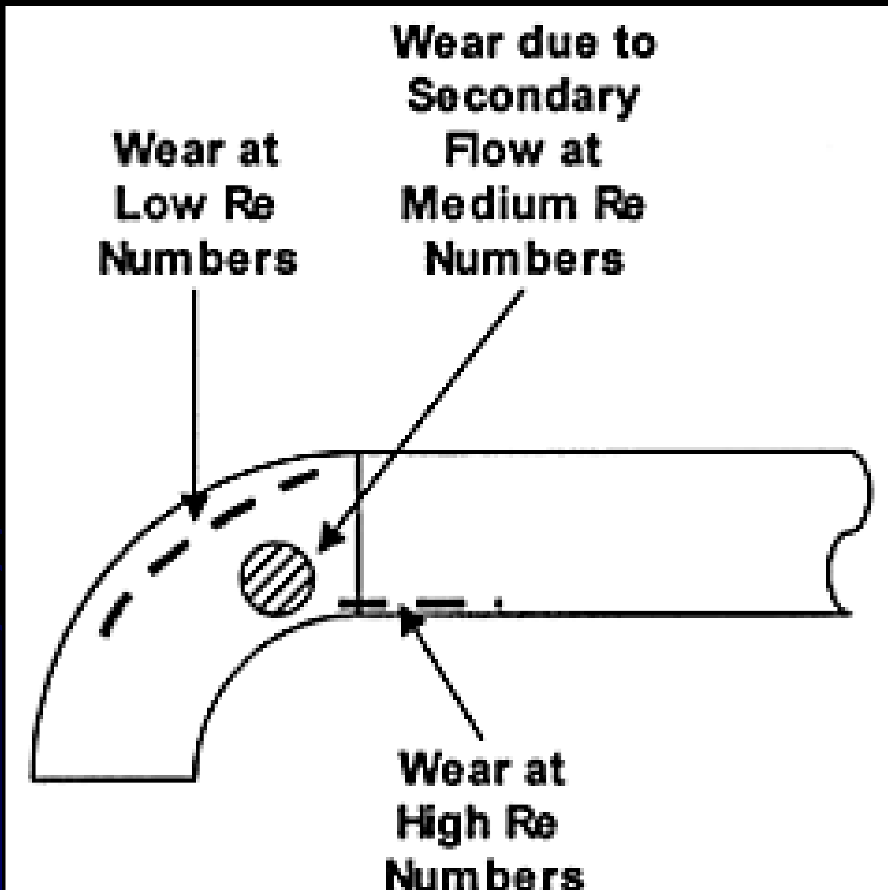
Dissolved oxygen (DO) concentration has a direct impact of the potential for flow assisted corrosion. Above a DO concentration of 30 mg/L (ppb), the normalized wear rate on carbon steel is at a minimum. Below 30 mg/L (ppb) DO, the normalized wear rate on carbon steel increases exponentially, as depicted in figure.

Effect of velocity on FAC



It only stands to reason that the mass velocity will have a significant influence on flow-assisted corrosion. Below 10 ft/sec (3.05 M/sec), the normalized wear rate is minimal, increasing 2.8 times at 100 ft/sec (30.5 M/sec).

Effect of geometry



Geometry, or general layout of the piping systems has an effect on the location of FAC, regardless of the Reynold's Number (Re). Consequently, changes in flow rate may not significantly reduce FAC. Figure shows areas of wear at different Reynold’s Numbers

Effect of metallurgy on FAC

- Flow assisted corrosion is most often found in systems with all ferrous metallurgy.

- The incorporation of as little as 0.1% chromium into low carbon steels has been shown to have benefits in reducing FAC

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AIM OF BOILER WATER TREATMENT

- THE MAGNETITE LAYER IS TO BE MAINTAINED- PREVENT CORROSION.

- PREVENT DEPOSITION OF SOLIDS FROM WATER-PREVENT OVEHEATING & CORROSION.

- PREVENT CARRYOVER OF SOLIDS TO STEAM- PREVENT OVERHEATING OF SUPERHEATER & TUBRINE BLADE DEPOSITS.