

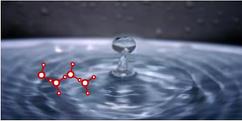


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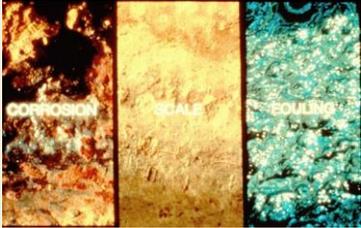
BOILER WATER TREATMENT INTRODUCTION

Bruce Ketrick – Guardian CSC



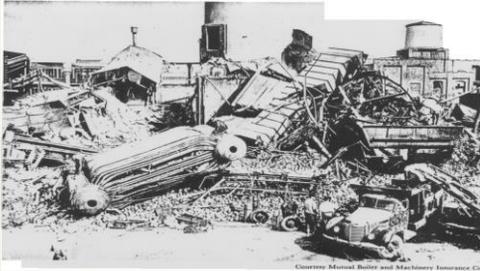


HOW CAN WATER HURT YOU?





This Was The Original Reason For Boiler Water Treatment





• CATIONS (POSITIVE CHARGE)

- HYDROGEN H⁺
- SODIUM Na⁺
- CALCIUM Ca⁺⁺
- MAGNESIUM Mg⁺⁺
- IRON (FERROUS) Fe⁺⁺
- IRON (FERRIC) Fe⁺⁺⁺
- ALUMINUM Al⁺⁺⁺



ANIONS (NEGATIVE CHARGE)

- ORTHOPHOSPHATE PO₄ [≡]
- SULFITE SO₃ [≡]
- SULFATE SO₄ [≡]
- CARBONATE CO₃ [≡]
- BICARBONATE HCO₃ ⁻
- HYDROXIDE OH ⁻
- CHLORIDE Cl ⁻

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PRETREATMENT



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EXTERNAL TREATMENT

Clarification
↓
Filtration
↓
Ion Exchange

↓

Sodium Zeolite Softeners Ultrapure Reverse Osmosis Demineralizers Dealkalizers

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EXTERNAL TREATMENT COMPONENTS



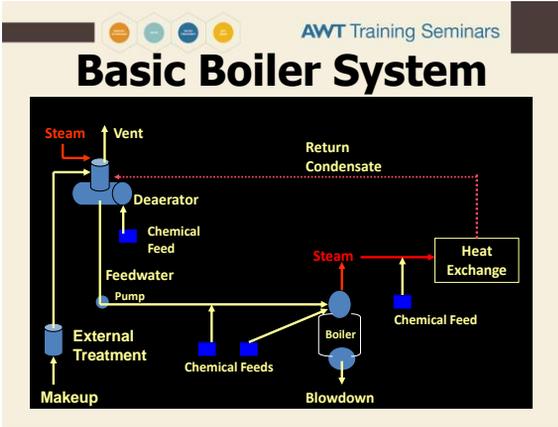
Filtration



Water Softener



Reverse Osmosis



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OXYGEN & DEAERATION



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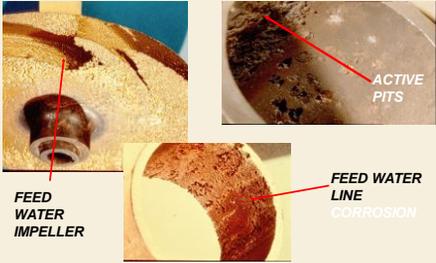
FEED WATER – OXYGEN REMOVAL

Oxygen is removed from the make up water in the feed water system. Dissolved gasses are driven off to varying degrees by increasing the temperature of the water..

Labels in diagrams: 60°F, 200°F, DEAERATOR

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Oxygen Pitting Corrosion



FEED WATER IMPELLER

ACTIVE PITS

FEED WATER LINE CORROSION

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Feed Water pH

- The pH of the feed water should be above 8.5 to prevent corrosion of iron in the system
- The pH of the feed water should be below 9.2, to prevent copper loss in the system
- Optimum pH in the feed water should be 8.5-9.2

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Deaerator Ratings

- Deaerators are categorized by the quantity of oxygen that they are able to remove at boiling point. The categories are;
 - Preheat Boiler Feed (Atmospheric Feed Water Tank)
 - 195° - 205°F (0.1 – 1 ppm Oxygen)
 - 0.03 DA Pressurized (**within 3°F of saturation**)
 - 44 ppb Oxygen remaining
 - 0.005 DA Pressurized (**within 3°F of saturation**)
 - 5- 7 ppb Oxygen remaining

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Factors For DA Operation

- **Temperature** – Increased temperature improves removal of dissolved gasses
- **Turbulence** – Required to scrub gasses out of the water
- **Time** – Efficiency is a function of time
- **Thin Film** – Increases the surface area of the water, which improves efficiency, the reason for trays
- **Transients** – The addition of fresh cold make up water to the system and the method used to maintain the boiling point in the DA to maintain efficiency.
- **Venting** – Must be a straight run. Elbows reduce the efficiency of the deaeration. Check the fixed plate orifice on pressurized units
- **Vent Condensing** – The DA's economizer

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Atmospheric Feed Water Tank

Water temperature is important for oxygen removal. With this system, the temperature limitation is feed water pump cavitation. When the feed water pump activates, the boiling point of water is reduced

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Feed Water Tank Specifications

- Feed water tank is an atmospheric tank.
- Oxygen scavenger is to be fed to the water section of the tank using a stainless steel quill.
- In that water temperature is important for the removal of oxygen. This tank needs to be as hot as possible.
- The problem with this type of system in particular is that if the tank temperature is held above 190° F there is a potential for feed water pump cavitation.
 - Temperature gauges fail, so holding the tank at 200°F.
 - When the feed water pump comes on, the boiling point of water is reduced
 - Deaerators use head pressure (1 psi for every 2.3 feet of height above the pump), where a feed water tank is barely 3 feet above the feed water pumps.
 - Watch the temperature closely to prevent pump loss due to cavitation.

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Condensate inlet and Make Up line are close together. This will cause pitting unless the valve and the "T" are replaced with Stainless Steel.

SPRAY-TYPE DEAERATOR.

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HORIZONTAL SPRAY-TYPE DEAERATOR.

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What is The Surge Tank?

- Used to control transient heat migration
- Can be used as a feed water tank and feed the boiler in lieu of the DA
- Can be an integral part of the DA (two compartment design) or free standing two tank system.
- Must be vented to allow oxygen to be removed
- Should be heated to maintain a minimum of 180°F with either an internal coil or a steam sparging line.

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When Is A Surge Tank Used?

- General Rule of Thumb
 - Systems with 80% or more of make up do not require a surge tank
 - Systems with more than 20% condensate returns, require a surge tank for effective uninterrupted deaeration.

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Two Tank DA System

On-Off operation causes any oxygen present to release suddenly when it comes on and causes pitting.

Transition Piping

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Dual Tank Systems - DA

- Dual tank systems have the condensate and the make up water blend in the first tank. This tank is heated only from the condensate and is not vented
- The concept is to provide less thermal shock to the system

- Problem is that rapid corrosion occurs in the initial tank and in the transfer lines.
- This should be made out of Stainless Steel.

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Water Problems Two Tank System

- In a two tank system, the first tank receives the condensate and the make up water.
 - The first tank is the Transient section that buffers the system from causing a temperature drop in the DA section.
 - Water temperature can be as low as 150°F. You want the temperature to be 180° F or above to minimize oxygen content.
 - Oxygen content is based on water temperature, so this tank has to be treated for oxygen before the system can mechanically deaerate. At 150°F Sodium Sulfitte has limited effectiveness.
 - With low temperatures and high oxygen content, the corrosion rate on carbon steel can be excessive.
 - The first tank must be vented or the first tank and the transition piping will corrode.
- Chemical treatment potentially filming amines, molybdate or tannins
- Oxygen is the corrosion inhibitor for quality stainless steel (316L – low carbon), so the construction of the first tank and related piping should be stainless steel.
- Feed water pump should be continuous run with return line to the DA instead of on/off to prevent sudden oxygen release in the piping.

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Cavitation – Feed Water Explosion

Cavitation is caused when feed water reverts to steam in the feed water pump. Bubbles of steam form in an explosive manner which cause physical damage to the feed water pump internals.

The Feed Water pump is designed to pump liquids, not steam, so it cavitates. This surging sound is distinctive.

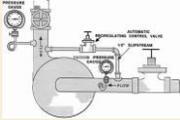



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Cure For Cavitation of Feed Water Pumps

- Cavitation is caused by the sudden release of steam in the feed water.
- A Deaerator is placed above the feed water pump, this creates head pressure over the pump. At 1 psi of head for every 2.3 feet of height, 30 feet \approx 13 psi of head pressure.
- In a system with a feed water tank instead of a DA, maintain the temperature below 200°F

The slip stream system uses a side stream to recirculate feed water back to the suction side of the pump, alleviating steam release (cavitation) in the feed water pump.



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DA Chemical Problems

- **Hardness** – Over 200°F the solubility of calcium carbonate hardness is 14 ppm. If hard water is allowed to go to the DA, it can flash deposit in the DA and migrate to the shaft of the feed water pump causing the shaft and packing to fail.
- **Injection Quill** – Always use stainless steel as sodium sulfite can dissolve iron at the point of injection.
- **Alkaline Products** – Adding an alkaline product to the DA will cause the catalyst in the sodium sulfite to drop out and can cause loss of copper in the impeller and the feed water check valve.
- **Iron** – Caused by poor return line treatment program or insufficient oxygen scavenger level.

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Oxygen Scavenger Tips- Part 1

- If the Deareator (DA) water temperature is within 3°F of the saturation, the oxygen content in the feed water should be 5-7 ppb.
- Remember when we talk about oxygen, gasses are referred to as volume to volume
- It takes 10-15% of steam by weight of make up to bring the feed water temperature up to within 3°F (1.7°C) of saturation
- DA **venting flow rate** is based on oxygen content of the feed water. Hence, percentage of make up can change the venting flow rate of a DA.

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Oxygen Scavenger Tips- Part 2

- Oxygen scavengers when applied properly, should be able to remove oxygen down to **1-3 ppb** by volume
- **The Law of Mass Action:** Excess feed of a reactant is used to drive a reaction to completion. Therefore, we maintain chemical residuals as Sodium Sulfite to force the reaction to completion
- Oxygen's ability to react with iron doubles every 10°C (18°F) increase in feed water temperature.



Oxygen Scavenger Tips- Part 3

- The pH of a solution of Sodium Sulfite in a mix tank should be below 8.5 to prevent the cobalt catalyst from precipitating out.
 - A 10% sodium sulfite solution in a mix tank will have a pH of approximately 8.5
 - Plugging of sodium sulfite mix tank chemical pumps and lines is usually precipitated cobalt sulfate catalyst.
 - Addition of 3.0% sodium bisulfite to sodium sulfite powder mix will keep mix tank pH below 8.0 where you have a 10% mix tank solution.



Oxygen Scavenger Tips- Part 4

- **Oxygen Solubility in Water**
 - The greater the pressure, the greater the solubility
 - The greater the temperature, the lower the solubility.
- **Oxygen Attack is prevented in the boiler system using;**
 - Oxygen scavengers as sodium sulfite
 - System passivators as DEHA, Hydrazine, Hydrazine substitutes, and Hydroquinone



Saturated Steam

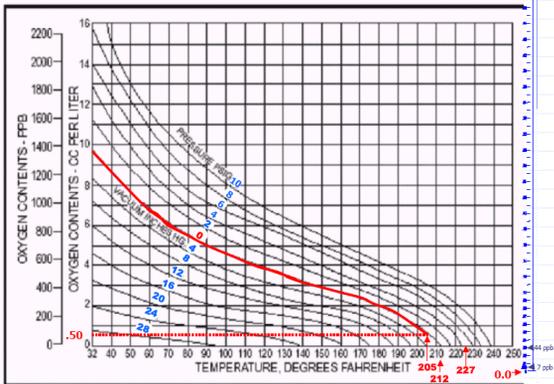
- **The efficiency of a feed water system is measured in it's ability to mechanically bring the feed water up to the saturated steam temperature.**
- **The saturated steam temperature is the point where the feed water exists as liquid and gas. Staying within 3°F of the saturated steam temperature maximizes the efficiency of the deareator.**



Saturated Steam Table

Pressure Lbs./Sq.In.	Temp. ° F	BTU per Lb.
- 0	212	180
- 2	218	187
- 4	224	190
- 6	230	198
- 8	235	203
- 10	239	208
- 12	244	210

Oxygen Solubility Graph





Oxygen Scavengers

- Sodium Sulfite
- Hydrazine
- Hydroquinone
- Carbohydrazide
- DEHA (N,N-Diethylhydroxylamine)
- Methylethylketoxime
- Erythorbic Acid



Introduction to Sodium Sulfite

- Sodium Sulfite reacts chemically with dissolved oxygen, producing sodium sulfate.
- Sodium sulfite is introduced continuously to the feed water system (**the storage section of the feedwater heater or deareator, six inches below the water line**).
- Chemical residual control is based on the maintenance of a specific excess of sodium sulfite in the boiler water.
- Optimum pH range for sodium sulfite to react to form sodium sulfate is **9.0 – 10.0**



Sodium Sulfite - Limits

- Maximum and minimum limits are specified for control of sodium sulfite in the boiler. You can increase or decrease the feed of this chemical, as necessary, in order to keep sulfite concentrations between the specified limits.

• Boiler Pressure	Sodium Sulfite Residual
• 0 – 150 psi	30 – 60 ppm
• 150 – 300 psi	20 – 40 ppm
• 300 – 600psi	20 – 30 ppm
• 600 – 900 psi	10 – 15 ppm
• 900 – 1200 psi	5 – 10 ppm
• 1500 psi	Sodium Sulfite Not Recommended



Catalyzed Sodium Sulfite Feed

- Catalyzed sodium sulfite (using cobalt sulfate) reacts more rapidly than uncatalyzed sodium sulfite.
- Catalyzed sodium sulfite must be fed by itself with a separate chemical feed system.
- Other boiler water chemicals are alkaline in nature and when they are mixed with catalyzed sodium sulfite, the alkalinity reacts and causes the cobalt sulfate catalyst to drop out.
- Catalyzed sodium sulfite should be fed through a stainless steel feed quill into the storage section of the deareator approximately 6" below the operating water level of the storage section.

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Sodium Sulfite Demand

- Primary demand for Sodium Sulfite in a boiler is to tie up free oxygen, not to develop a residual
- Sodium Sulfite demand can be increased by:
 - Drop in temperature in the feed water system
 - Leaving the sodium sulfite tank mixer on (aerates solution)
- If deareator temp is within 3°F of saturation, oxygen content is 5-7 ppb, yet a temp of 170°F in a feed water tank can have an oxygen content as high as 2 ppm.
- Unheated make up water may contain from 6 – 8 ppm of oxygen

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Sodium Sulfite Demand

- Calculation for sodium sulfite demand is
 - $(10 \times \text{Dissolved Oxygen}) + [(\text{Residual} \times 1.6) \div (\text{Feed Water Cycles})]$
 - Assuming 40 feed water cycles and a 40 ppm desired residual
 - If D.O. is 0.001, Sulfite demand is 1.61 ppm
 - If D.O. is 0.01, Sulfite demand is 1.7 ppm
 - If D.O. is 0.1, Sulfite demand is 2.6 ppm
 - If D.O. is 1, Sulfite demand is 11.6 ppm

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Hydrazine

- Hydrazine is used as an oxygen scavenger in high-pressure systems. It does not contribute solids to the boiler.
- It is listed as a **known carcinogen (OSHA PEL 0.1 ppm, subject to SARA Title III Section 313 reporting) and requires special handling.**
- Hydrazine comes as a 35% liquid and is **to be fed directly from the container into the feed water system, at a rate of 0.05 – 0.10 ppm.** The addition of Hydroquinone to hydrazine increases the reaction time of the hydrazine from 10 – 100 times. The Hydrazine reaction is one of the slowest of the oxygen scavengers where it is not catalyzed and the water temperature is below 300° F.
- In temperatures above **750° F Hydrazine begins to break down into ammonia** which is corrosive to yellow metals.



Hydroquinone (C₆H₄(OH)₂)

- Hydroquinone is 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.
- Hydroquinones are toxic. "Aqua Toxins"
- When using a mixed bed demineralizer, the rapid reduction reaction of this product will cause the resin to turn black. This can become a problem during regeneration where the ability to visually see the separation of the resin is important.
- Hydroquinone is stable up to 572° F were it begins to break down. 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.**



Carbohydrazide (N₂H₃)₂CO CHZ

- This is a hydrazine substitute. A product that acts like hydrazine without the same hazards as hydrazine.
- Nalco Elimin-Ox is a carbohydrazide. Expired patent (#4,269,717)
- CHZ does not contribute to the boiler solids. It reacts at a rate of **1.4 ppm of CHZ for every 1 ppm of oxygen.** 1.4 ppm will form an additional **0.7 ppm of CO₂.** Take this into account when calculating the neutralizing amine requirement.
- The material is usually sold as a 6.5% solution. It is fed to the feed water system to be **controlled at 0.05 to 0.3 ppm as Hydrazine.**
- CHZ will decompose into the same byproducts as Hydrazine.



DEHA (CH₃CH₂)₂NOH N,N-Diethylhydroxylamine

- DEHA is a volatile oxygen scavenger, sold as an 85% or 25% liquid. It has the ability to passivate the metal surfaces in the boiler, then pass out of the boiler with the steam, and act as a metal passivating agent in the return line system.
- DEHA can be **catalyzed with either a copper salt or Hydroquinone.** The feed rate of the DEHA is 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.**



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DEHA (CH₃CH₂)₂N₂OH

- **150 – 300 ppb** in the boiler, the DEHA reaction also forms some acetic acid. This is neutralized to acetate in the boiler and then eventually breaks down into carbon dioxide. This must be taken into account when reviewing the neutralizing amine program. You will also find some decomposition of the DEHA into ammonia. This does not occur until you have reached 534° F as compared to Hydrazine break down to ammonia at 334° F.
- DEHA is a strong reducing agent that is capable of reverting reddish ferric oxide into magnetite in the boiler. Concentrations of **have proven to be effective to protect boiler metal surfaces from corrosion**
- DEHA test uses iron as it reacts with ferric iron to form ferrous iron **Residual can be controlled between 0.5 – 1.0 ppm.**



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DEHA (CH₃CH₂)₂N₂OH

- DEHA is controlled based on testing the Feed Water and the Condensate.
- Initial Start Up Control range in the (Deaerator) Feed Water could be 50 – 75 ppb.
- Target range in the condensate would then be 10 -20 ppb
- Conservative start up dosage would be 300- 500 ppb with condensate ranges at 80 – 120 ppb
- Normal system control range is 0.5 – 1.0 ppm
- Reaction with Oxygen forms acetic acid which then becomes an acetate salt in the boiler, leaving with blow down
- $4(\text{CH}_3 \text{CH}_2)_2\text{NOH} + 9 \text{O}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{N}_2 + 6\text{H}_2\text{O}$



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Methylethylketoxime (CH₃CNOCH₂CH₃) 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.
- MEKO has the fastest reaction time of any sodium sulfite substitute. It is fed neat from a 100% solution to the feed water at a rate of **5.4 ppm of MEKO for every 1 ppm of oxygen**. The control of the product is; **0.8 – 1.2 ppm in the system using an iron reduction test.**
- **MEKO does not have passivation capabilities**, so it is not recommended for use in lay up.
- MEKO Toxicity data: **MEKO** 2-Butanonoxim (CAS-Nr.: 96-29-7) is labeled as **Risk of Cancer** (H351)



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Erythorbic Acid (Erythorbate) (C₆H₈O₆)

- 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.
- 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.
- Excellent for iron transport in a system.

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Erythorbic Acid (Erythorbate) (C₆H₈O₆)

- EA is catalyzed with transition metals, like sodium sulfite. Also, if you have **1 ppb of iron in the feed water, it can 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.*
- EA is controlled at 0.5 – 1.0 ppm using a Colorimeter
- 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, that assists in magnetite formation. It is believed that break down products from the EA sequester iron and then form magnetite on the metal surface.

Oxygen Scavenger Note: CR is for 100% scavenger	Combine Ratio Practical	Max Pressure psig	Volatility/ Distribution Ratio	Passivation ability
Sodium sulfite, solid or 10% soln. Cat. = Co or Eryth.	10:1 Rapid scavenger	950 max. Risk of SO ₂ /H ₂ S	Not volatile DR = Nil	Limited, only over 300 psig
Sodium bisulfite, 40% soln. Cat. = Co or Eryth	7:1 Rapid scavenger	950 max. Risk of SO ₂ /H ₂ S	Not volatile DR = Nil	Limited, only over 300 psig
Na metabisulfate 100% Cat. Co or Eryth.	5:1 Rapid scavenger	950 max. Risk of SO ₂ /H ₂ S	Not volatile DR = Nil	Limited, only over 300 psig
Hydrazine, 15 or 35% soln. Cat. = HQ	3:1 Rapid scavenger	2500+ Produces NH ₃	Poor volatility DR = 0.1	Excellent for all system
DEHA as 17.5 to 30% soln. Cat. = HQ or Cu	3:1 Rapid scavenger	2500+ Some NH ₃	Good volatility DR = 1.3	Excellent for all system
Erythorbate 10 to 20% soln. Cat. = Cu/NI/Fe	10:1 Good scavenger	1500 Nothing harmful	Not volatile DR = Nil	OK, but only in the boiler
Hydroquinone 15/25% soln. Cat. = pyrogallol	7:1 Scavenger enhancer	1500 Produces CO ₂	Only at 1500 psig DR = 0.15	Acts as enhancer only
MERKO Poor solubility Cat. = Erythorbate	6:1 Weak scavenger	1250 Risk of charring	Highly volatile DR = 2.2	No true ability to passivate
Carbohydrazide, 6.5% soln. Cat. = Cu or Co	1.5 Slow scavenger	2500+ Produces CO ₂ /NH ₃	Some, but only over 130 psig	Excellent but only utilities
1-Aminopyrrolidine as 30% soln Cat. = HQ	2:1 OK scavenger	1250 Risk of charring	Some volatility DR = 0.7	OK, but not special
Tannins 25-50% soln. Cat. = None or Eryth.	10:1 Good for cold FW	650 max. Product then fails	Not volatile DR = Nil	Excellent but only in boiler



Alternate Chemistry - Oxygen Protection

• Tannins

- Functions as a filming agent on metal surfaces.
 - Functional group is a reaction with the free iron to form a complex on the metal surface. Absorption followed by magnetite formation
 - Quebracho is the most important tannin source with a high level of the hydrolyzable tannin pyrogallol (when in an alkaline state, this absorbs oxygen turning purple), and Quinic acid which produces Hydroquinone another oxygen scavenger
 - Tannins are long chain aliphatic polyanions, which gives them dispersant properties as well as adsorption of hardness ions.



Alternate Chemistry - Oxygen Protection

• Tannins

- Tannin products are blends of other plant derivative tannins as Wattle and Mimosa which assist in dispersion.
- Tannin does not volatilize out of the boiler, so ammonia is usually added to a tannin package to assist in return line.
- Tannins adsorb onto copper and other yellow metals, have been used for aluminum boiler systems.
- Cautions for product applications are;
 - Irregularities in complex may leave surface areas open for localized corrosion.
 - Direct replacement to synthetic dispersants may require excessive feed rates.
 - Tannin discharge maybe monitored as nutrient source.



Alternate Chemistry - Oxygen Protection

• Filming Amines

- Blended filming amines function by coating the surfaces of the metal surface.
 - Coating prevents oxygen from contacting metal surfaces
 - Use tallow, soy bean and a volatile filming amine to carry into the boiler and out to the condensate system
- Blend of volatile and nonvolatile filming amines
- Function similar to Tannin as the hydrophobic end adsorbs to the metal surface, lifting debris
 - Octadecylamine $\rightarrow n=0, R_1 = C_{18}H_{37}$
 - Oleyldipropyldiamine $\rightarrow n = 1, R_1 = C_{18}H_{35}, R_2 = C_3H_7$
 - Oleylamine $\rightarrow n=0, R_1 = C_{18}H_{35}$
- Oleylamine enhances heat transfer on boiler surfaces

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Cycles of Concentration

- Cycles refer to the concentration of solids in the boiler water.
- As the water is evaporated, the solids stay behind. These solids are now more concentrated, or cycled up



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The Quality of The Water Determines How Many Cycles We Can Run In The Boiler

ASME WATER QUALITY GUIDELINES

DRUM PRESSURE (psi)	BOILER FEED WATER			BOILER WATER		
	Iron (ppm Fe)	Copper (ppm Cu)	Total Hardness (ppm CaCO3)	Silica (ppm SiO2)	Total Alkalinity (ppm CaCO3)	Conductivity (Unneutralized)
0-300	0.1	0.05	0.3	150	700	7000
301-450	0.05	0.025	0.3	90	600	3500
451-600	0.03	0.02	0.2	40	500	3800
601-750	0.025	0.02	0.2	30	200	1500
751-900	0.02	0.015	0.1	20	150	1200
901-1000	0.02	0.01	0.05	8	100	1000
1001-1500	0.01	0.01	Not Detectable	2	Not Specified	150
1501-2000	0.01	0.01	Not Detectable	1	Not Specified	80

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ASME Water Tube Feed Water Limits

Feed Water	UNIT	0-300 psi	301-600 psi
Oxygen (No OS)	Mg/l O2	<0.007	<0.007
Total Iron	Mg/l Fe	<0.10	<0.05
Total Copper	Mg/l Cu	<0.05	<0.025
Total Hardness	Mg/l CaCO3	<0.5	<0.3
PH Range		8.3 – 10.5	8.3 – 10.5
Nonvolatile VOC	Mg/l C	<1	<1
Oily Matter	Mg/l	<1	<1

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ASME Water Tube Boiler Control Limits

<u>Boiler Water</u>	<u>UNIT</u>	<u>0-300 psi</u>	<u>301-600 psi</u>
Silica	Mg/L SiO ₂	<150	<90
Total Alkalinity	Mg/l CaCO ₃	<1000	<850
Free OH	ppm	NS	NS
Un-neutralized Conductivity	Mmhos/cm	<7000	<5500
Steam Purity	Solids	1 ppm	1 ppm

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ASME Fire Tube Boiler FW Limits

<u>Feed Water</u>	<u>UNIT</u>	<u>0-300 psi</u>
Oxygen (No OS)	Mg/l O ₂	<0.007
Total Iron	Mg/l Fe	<0.10
Total Copper	Mg/l Cu	<0.05
Total Hardness	Mg/l CaCO ₃	<0.1
PH Range		8.3 – 10.5
Nonvolatile VOC	Mg/l C	<10
Oily Matter	Mg/l	<1

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ASME Fire Tube Boiler Limits

<u>Boiler Water</u>	<u>UNIT</u>	<u>0-300 psi</u>
Silica	Mg/L SiO ₂	<150
Total Alkalinity	Mg/l CaCO ₃	<700
Free OH	ppm	NS
Un-neutralized Conductivity	Mmhos/cm	<7000
Steam Purity	Solids	1 ppm

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American Boiler Manufacturers Association ABMA Boiler Water Limits

- Boiler pressure 0-300 psi
- Silica 180 ppm @ SiO₂
- Total Hardness 500 ppm Fire Tube Boiler or 300 ppm for Water Tube Boiler
- Total Alkalinity 900 ppm
- Neutralized Conductivity TDS 3500 ppm

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Determination of Boiler Cycles

<ul style="list-style-type: none"> • Make up water <ul style="list-style-type: none"> - 200 mmhos conductivity - 50 ppm total alkalinity - 6 ppm silica - 100 ppm total hardness • Calculations <ul style="list-style-type: none"> - Conductivity - Total Alkalinity - Silica - Total Hardness Firetube - Total Hardness Watertube 	<table border="0"> <tr> <td style="text-align: right;">Allowable limits</td> <td></td> </tr> <tr> <td></td> <td style="text-align: right;">3,500 mmhos</td> </tr> <tr> <td></td> <td style="text-align: right;">900 ppm</td> </tr> <tr> <td></td> <td style="text-align: right;">180 ppm</td> </tr> <tr> <td></td> <td style="text-align: right;">300 or 500 ppm</td> </tr> </table> <table border="0"> <tr> <td style="text-align: right;">3500/200 =</td> <td style="text-align: right;">17.5</td> </tr> <tr> <td style="text-align: right;">900/50 =</td> <td style="text-align: right;">18</td> </tr> <tr> <td style="text-align: right;">180/6 =</td> <td style="text-align: right;">30</td> </tr> <tr> <td style="text-align: right;">500/100 =</td> <td style="text-align: right;">5</td> </tr> <tr> <td style="text-align: right;">300/100 =</td> <td style="text-align: right;">3</td> </tr> </table>	Allowable limits			3,500 mmhos		900 ppm		180 ppm		300 or 500 ppm	3500/200 =	17.5	900/50 =	18	180/6 =	30	500/100 =	5	300/100 =	3
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Limiting factor is hardness, so cycles are either 5 or 3

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Importance of a Water Softener for Boiler Cycles

<ul style="list-style-type: none"> • Make up water <ul style="list-style-type: none"> - 200 mmhos conductivity - 50 ppm total alkalinity - 6 ppm silica - 1 ppm total hardness • Calculations <ul style="list-style-type: none"> - Conductivity - Total Alkalinity - Silica - Total Hardness Firetube - Total Hardness Watertube 	<table border="0"> <tr> <td style="text-align: right;">Allowable limits</td> <td></td> </tr> <tr> <td></td> <td style="text-align: right;">3,500 mmhos</td> </tr> <tr> <td></td> <td style="text-align: right;">900 ppm</td> </tr> <tr> <td></td> <td style="text-align: right;">180 ppm</td> </tr> <tr> <td></td> <td style="text-align: right;">300 or 500 ppm</td> </tr> </table> <table border="0"> <tr> <td style="text-align: right;">3500/200 =</td> <td style="text-align: right;">17.5</td> </tr> <tr> <td style="text-align: right;">900/50 =</td> <td style="text-align: right;">18</td> </tr> <tr> <td style="text-align: right;">180/6 =</td> <td style="text-align: right;">30</td> </tr> <tr> <td style="text-align: right;">500/1 =</td> <td style="text-align: right;">500</td> </tr> <tr> <td style="text-align: right;">300/1 =</td> <td style="text-align: right;">300</td> </tr> </table>	Allowable limits			3,500 mmhos		900 ppm		180 ppm		300 or 500 ppm	3500/200 =	17.5	900/50 =	18	180/6 =	30	500/1 =	500	300/1 =	300
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Limiting factor is conductivity, so cycles are 17.5

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Hot Water Boilers

- Hot Water Boilers fall into three general categories;
 - Caste Iron Boilers
 - Hot Water Closed Loops
 - Electric Boilers

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Caste Iron Boilers

- Caste Iron Boilers
 - Either gasket or push nipple
 - Gasket boilers can not use products that contain caustic materials, so use **10% sodium sulfite with 5% polymethacrylate** and control at 100 - 150 ppm as sodium sulfite
 - Always put a water softener in front of a caste iron boiler. These boilers have poor circulation rates, so they can not handle the precipitation that hard water or precipitation chemistry would cause.
 - Where the unit is a steam boiler, amine use is only in push nipple.
 - Tannins or Blended Filming amines may be considered.

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Hot Water Closed Loop & Electric Boilers

- Hot water Closed Boilers can be treated with a sulfite/polymer products or with simple Nitrite/Borate/Silica product with control at 600 - 1000 as Nitrite.
- Electric Boilers must have low conductivity or they will arc. Use DEHA or DI make up with very low sulfite level. When using a sulfite program the addition of Erythorbate will assist the sulfite.

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Molybdate Treatment

- A concern in heating boilers with high levels of condensate return and low blow down, is the potential for oxygen pitting. This can also occur in dual tank deaerators.
- Molybdate chemistry can be effective in these cases.
- Product should contain Molybdate, DEAE (Diethyl aminoethanol), caustic soda, polyphosphate and a dispersant.

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Molybdate Program

- Feed to obtain
 - 125 – 250 ppm as MoO₄ (Molybdate) or 75 – 150 ppm as Mo+6 (Molybdenum).
 - 20 – 40 ppm as PO₄
 - 200 ppm OH Alkalinity
 - Condensate pH of 7.5 – 9.0
- This is for seasonal long term storage, systems that are not tested regularly and where sulfite has not proved effective
- Limit the use to boilers pressures under 150 psi and hot water boilers operating under 350°F.

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BOILER TYPES AND DESIGNS






Boiler Design





After Pretreatment and Deaeration, We Come to the Boiler



Fire Tube Dry Back Boiler



Fire Tube Wet Back Boiler



Fire Tube Boiler Internals Combustion Gas



The internal design of a fire tube boiler starts with the combustion in the center fire tube or Morrison tube.

The heat from combustion hits the rear door where it is directed back to the front of the boiler.

Then, combustion gasses are redirected back to the rear of the boiler.

Each time the combustion gas is redirected, it is considered a pass. The more passes a boiler makes, the more heat the boiler is able to remove from the combustion gasses. Hence the lower the stack exit temperature of the boiler.



Dry Back Vs Wet Back



Dry back boilers deflect the heat of combustion on a dry refractory back.

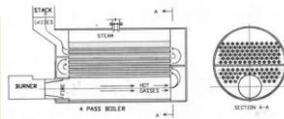
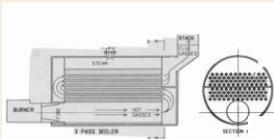
Caution when over heating the boiler



Wet Back boilers redirect the heat of combustion off of a wetted section picking up more heat at the end of the first pass and can take more over heating.

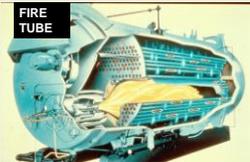


3 & 4 Pass Fire Tube Boiler Design





Fire Tube Boiler Internals Steam Generation



The steam that is made in the fire tube boiler rises out of the boiler water that is covering the boiler tubes.

[\2012\boiler.mov](#)

This steam then enters the dry box, or water separator in the boiler. Here a series of plates or chevrons cause the steam to make contact and change direction.

This contact or direction change mechanically separates water that is in the steam. Water then drops back into the boiler water to be used to form more steam.

Circulation rate is as important to keeping a boiler clean as any other part of the treatment program, so it is essential that the passes between the tubes are kept clean.

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Fire Tube Boiler Gas Train & Water Column Design

The diagram illustrates the gas train and water column design for a fire tube boiler. Key components include the burner, fuel gas regulator, gas pilot solenoid, gas pressure regulator, and various safety valves and switches. The water column is shown with a level control and a vent valve.

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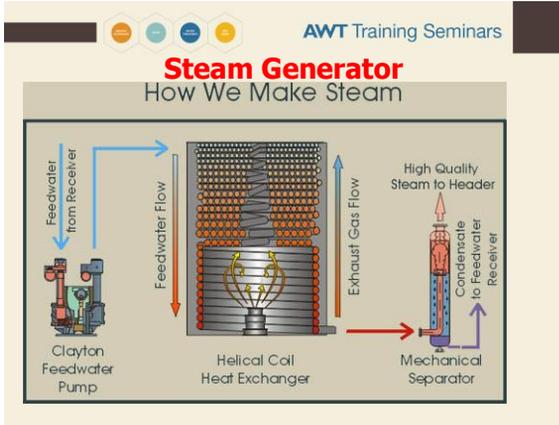
Cast Iron Sectional

The photograph shows a cast iron sectional boiler installed in a room. The boiler is a large, black, rectangular unit with various pipes and valves attached.

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Steam Generator

The photograph shows a steam generator, which is a large, cylindrical unit with a control panel on the side.





Tubeless Vertical Boiler

The diagram shows a cross-section of a tubeless vertical boiler. It features a central flame tube and an outer water jacket. Arrows indicate the downward flow of flame and the upward flow of water/steam.

Tubeless Vertical Boiler Internals

- Flame is directed down from the top of the boiler toward exhaust on the lower section.
- Water is located on the outside of the flame tube.
- Rapid formation of steam.
- Takes abuse well as it is basically a sophisticated kettle.
- Pretreat with soft water, blow down daily and use a dispersant with oxygen scavenger



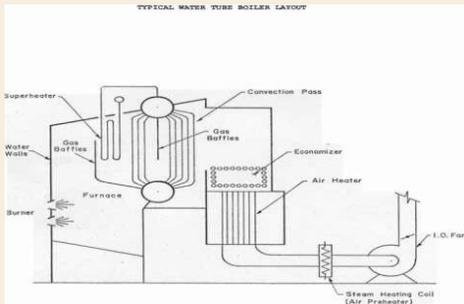
Hybrid Boiler





Water Tube Boiler Lay Out

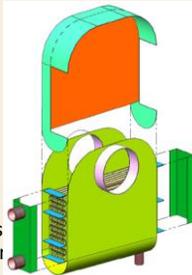
TYPICAL WATER TUBE BOILER LAYOUT





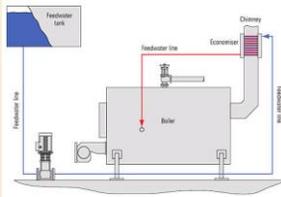
ECONOMIZER

- A boiler economizer is a heat exchanger device that captures the "lost or waste heat" from the boiler's hot stack gas.
- The economizer typically transfers this waste heat to the boiler's feed-water or return water circuit, but it can also be used to heat domestic water or other process fluids.
- Capturing this normally lost heat reduces the overall fuel requirements for the boiler.
- In Water Tube Boilers the economizer is located at the breaching or in the stack





ECONOMIZER



installation in round stacks



Mounting Flanges for Bolting to Mating Flanges or Adapters





ECONOMIZER

- As BTU's from the stack gas is absorbed by an economizer, that temperature of the feed water is increased.
 - This is a means of scavenging BTU's (Pay back from fuel savings)
 - It also causes deaeration of the feed water.
 - An Economizer not vented, so any oxygen released from the increase in temperature is available to cause pitting corrosion in the unit.
 - Protect the economizer from oxygen pitting by maintaining a **minimum of 5 ppm of catalyzed sulfite in the feed water.**
 - Test a feed water sample, taken upstream of the economizer for this test and control 5 – 15 ppm as sulfite.

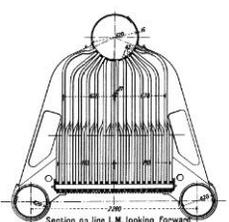


Water Tube Boiler Tubes



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Package Water Tube



"A" Type Boiler



"D" Type Boiler

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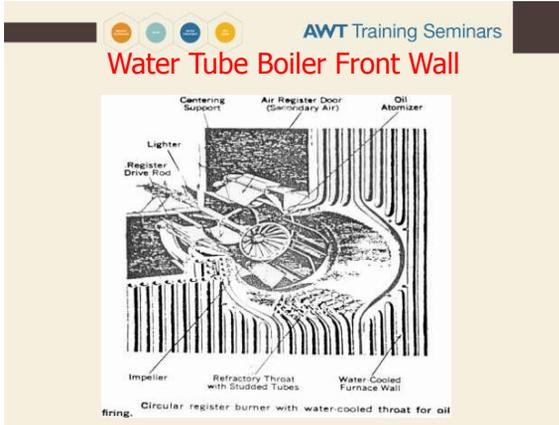
"A" Type Boiler Internal



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A Type Boiler – Internal Back to Front

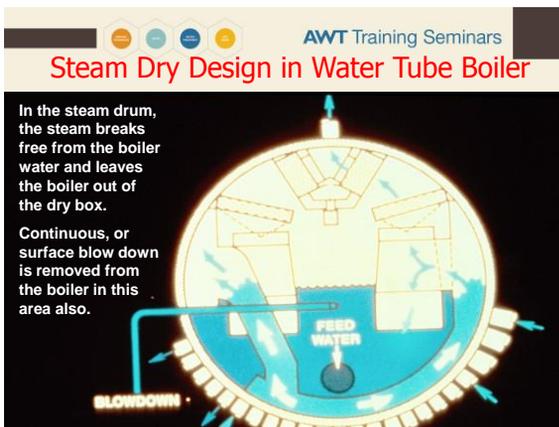




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Fire Side Temperatures And Problems

<u>LOCATION</u>	<u>GAS TEMP</u>	<u>OUTER METAL TEMP</u>	<u>DEPOSIT TEMP</u>	<u>PROBLEMS</u>
FLAME	2500-3100			Combustion
FURNACE	2000-2800	800	2000-2500	High temp corrosion, slag, spalling
SUPER HEATERS & REHEATERS	1200-2000	1000	1000-2000	High Temp corrosion, slag, fouling
CONVECTION	900-1200	500-900	1000	Fouling
ECONOMIZER	600-1200	200-600		Low Temp corrosion, fouling
AIR HEATER	300-600	200-500		Low Temp corrosion, fouling



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Water Tube Boiler Steam Drum Internals

Deflector Plates

Riser Tubes

Downcomer Tubes

Feedwater Line

Steam Release Area

Chemical Feed Line

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Steam Released In A Water Tube Boiler

Steam evolves in the boiler water. As it evolves, it rises in the riser tubes to release in the steam drum. Baffles and plates deflect the boiler water forcing it to fall back into the boiler, as the steam leaves the boiler

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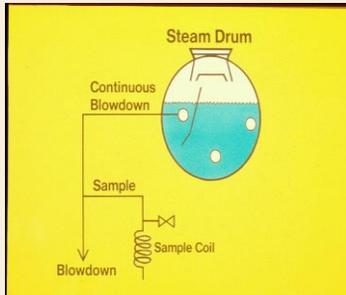
Water Tube Boiler Mud Drum

MUD DRUM

The mud drum is the lowest level of the water tube boiler. In the mud drum, solids in the water settle out and form sludge. This sludge is then removed from the boiler with manual blow down. Manual blow down should only be a succession of 5 second "puff" blows.



Continuous Blow Down



The *majority* of the blow down removed from a boiler should out of the Continuous blow down line.

This is primary control of the conductivity in the boiler.

The manual blow down from the mud drum should be for the removal of sludge, not the control of the solids level in a boiler.



Blow Down Valves & Piping

- Blow down piping should be at least the same size as the blow down tapping on the boiler.
- There should be either two slow opening valves or one quick opening and one slow opening valve on the blow down line.
- If there is one quick opening and one slow opening valve, the quick opening valve should be located closest to the boiler.
- If possible, blow down valves should be piped on the same side of the boiler as the water column gauge glass.
- A quick opening valve is a valve that opens or closes with one complete motion.
- A slow opening valve is defined as needing five complete 360 degree turns to go from fully closed to fully open



How To Blow Down A Boiler

- Open the quick opening valve first (one closest to the boiler)
- Open the slow opening valve last.
- Blow down the boiler for the required period of time (5 second puff blow). Pay close attention to the water level in the boiler, you may have to blow down the boiler several times if the boiler is starved for water.
- Close the slow opening valve first
- Close the quick opening valve last.
- Open the slow opening valve again to drain the line between the quick opening valve and the slow opening valve.
- Close the slow opening valve again and double check for tight shutoff after the valve has cooled off.
- NEVER pump the quick opening valve to blow down the boiler! This may cause water hammering, damage and injury.

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SCALE & DEPOSIT FORMATION

BOILER FAILURES



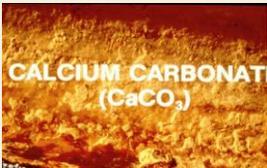
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Conductivity Is Used To Determine Blow Down

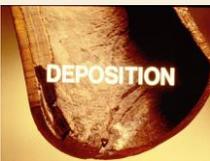
- Answer the following problem. Consider that the plant is using conductivity to determine blow down.
- A boiler is running at 80% load and has not been blown down for a week.
 - Conductivity in the boiler is dropping not rising
 - Alkalinity in the boiler is going up slowly
 - All manual and continuous blow down lines were checked and found to be cold, we are not losing boiler water there.
 - Why is the conductivity dropping instead of rising as it should?
- Clue: Plant recently changed the direction of flow in their water mains. Plant treats their own water from a stream.

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Scale; Insulates, Over Heats Tubes, Forms Readily



CALCIUM CARBONATE (CaCO₃)



DEPOSITION

Calcium Carbonate is inversely soluble in water as the water is heated up. In short, the hotter the water, the less calcium carbonate it will hold.

Once calcium carbonate precipitates out of the water, it migrates to hot surfaces and builds scale

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Deposit Formation

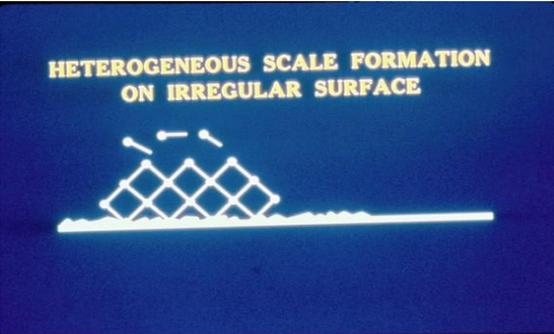


Once scale has formed on a metal surface, this deposit will attract other charged particles in the boiler water.



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HETEROGENEOUS SCALE FORMATION ON IRREGULAR SURFACE



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Tricalcium Phosphate Deposits



•Second only to calcium carbonate scale, tricalcium phosphate deposits are commonly found in boilers.

•Tricalcium phosphate is formed from improper phosphate treatment in the boiler



•Tricalcium phosphate deposits are formed by precipitation, so they may have a layered effect



Iron Deposits Are Denser than Calcium Deposits And Harder To Remove



- Iron based deposits in a boiler insulate the tubes more than calcium carbonate.
- They are much more difficult to remove than calcium based deposits.
- Iron comes from corrosion in the condensate system or from corrosion due to oxygen in the feed water.
- Control of the iron deposition in the boiler, requires corrosion control

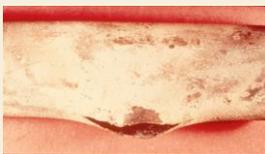
In the higher temperature zones of a boiler, the insulative effect from deposits cause the metal surfaces to become hotter than they are designed to withstand. The result is tube failure.

HIGHER TEMPERATURES

Remember, tube metal melts at 900°F and the tubes are supposed to operate below 600°F. Combustion gasses are 3200°F at the burner and drop as they pass through the boiler. Only the cooling effect of the boiler water prevents metal fatigue and tube failure.



Tube Failures Are Seen As Bursts



Water Tube Boiler deposits build up in the tubes causing thin or thick lip bursts. As the metal of the tube over heats, the tube bulges, then bursts. High temperature stress cracking, the tube over heats, becomes hardened steel which is brittle and cracks



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Tube Failures



Thin Lip Burst
Rapid
Overheating
Short Term



Thick Lip Burst
Long Term Chronic
Overheating
Usually Scale Related



**High Temperature
Stress Cracking**

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Boiler Water Treatment Must Protect The Boiler From Scale and Corrosion

CORROSION



SCALE



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Chloride Corrosion

- **Chlorides – High levels of chlorides can cause failure of stainless steel and other passivating films.**
 - Stainless steel is a blend of iron, nickel and at least 10.2% chromium (316 also contains Molybdenum)
 - Stainless steel forms a passive corrosion resistant film when oxygen combines with chromium to form a ceramic chrome oxide film
 - As little as 10 ppm of chloride can act to interrupt this film.
 - Welds are most susceptible as once the stainless steel has been heated over 1000°F, carbide migration occurs. Chlorides in contact with carbide migration cause intergranular corrosion
 - In most cases 200 ppm of chlorides or above can cause corrosion in stainless steel
 - As heat increases, the ability for chlorides to corrode stainless steel increases.
- **250 ppm of chlorides is usually sufficient to cause pitting corrosion on steel and coating disruption on galvanized**



Corrosion VS Erosion



Erosion is commonly mistaken for corrosion.

- Where corrosion is the loss of metal due to a chemical reaction that reverts the metal into an oxide form, erosion is simply water traveling at too high of a velocity in the system.
- Erosion is evident by the linear lines that correspond with the flow of the water.
- High solids content in the water will enhance erosion.
- Solutions to erosion are, increase line size, reduce flow rate and reduce solids in the water



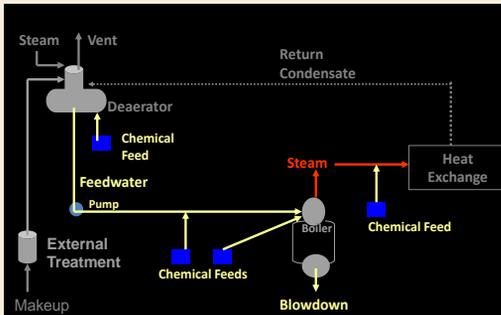
BOILER WATER CHEMICAL TREATMENT

PRODUCTS
PROGRAMS
APPLICATION





Chemical Feed Points



AWT Training Seminars

What Are The Three Basic Treatment Programs To Prevent Scale?

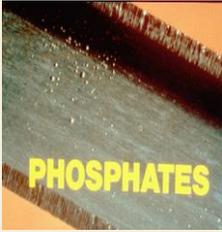
PRECIPITATING CHEMISTRY

CHELANT CHEMISTRY

ORGANIC PROGRAM

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Phosphate Treatment



- Phosphate is used in the boiler to prevent calcium carbonate scale.
- Phosphate reacts with calcium and the hydroxyl ion to form Hydroxyapatite. $[Ca_{10}(PO_4)_6(OH)_2]$.
- This is a soft, voluminous, light precipitant .
- The key is keep it in circulation while in the boiler and then get it out through blow down
- Insufficient hydroxyl ion allows, Tricalcium Phosphate to form $[Ca_3(PO_4)_2]$.

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Phosphate Reactions

- You need 20 ppm as orthophosphate for the precipitating orthophosphate program to become the primary reaction.
- Control orthophosphate in the boiler 20 - 60 ppm as orthophosphate
- Do not exceed 60 ppm of orthophosphate in the boiler or you will form magnesium phosphate complex which is a severe deposit.

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Phosphate Reaction Chemistries

Phosphate Conditioning: - under correct pH/alk conditions, reaction → *Hydroxyapatite* a mixed salt, with formula:
 $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$

$2Na_3PO_4$	$+ 3CaCO_3$	\rightarrow	$Ca_3(PO_4)_2$	$+$	$3Na_2CO_3$
TSP	calcium carbonate		tri-calcium phosphate		sodium carbonate

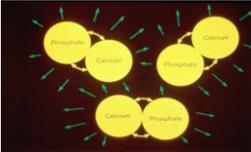
$2NaOH$	$+ CaCO_3$	\rightarrow	$Ca(OH)_2$	$+$	Na_2CO_3
sodium Hydroxide	calcium carbonate		calcium hydroxide		sodium carbonate

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Lack of Hydroxyl Ion = Tricalcium Phosphate Scale

Lack of Hydroxyl ion (OH), causes the phosphate in the boiler water to form a hard Tricalcium Phosphate scale.

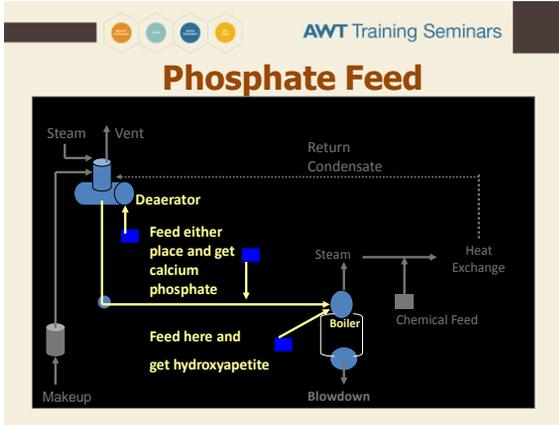
This can happen with soft water feed, so it is important to add the phosphate to the boiler where the alkalinity is present and to keep the alkalinity up in the boiler.




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Phosphate & Alkalinity

- When a water softener fails, the phosphate residual and the hydroxyl alkalinity are lost.
- Add caustic soda to bring up OH⁻ residual above 250 ppm
- Then add phosphate to form Hydroxyapatite.



Orthophosphate Contribution

PHOSPHATE	FORMULA	P ₂ O ₅ %	PO ₄ %
Disodium Phosphate	Na ₂ HPO ₄	48	66
Monosodium Phosphate	NaH ₂ PO ₄	58	79
Phosphoric Acid (75%)	H ₃ PO ₄	54	73
Sodium Hexametaphosphate	(NaPO ₃) ₆	68	93
Sodium Metaphosphate	NaPO ₃	69	94
Sodium Tripolyphosphate	Na ₅ P ₃ O ₁₀	58	78
Tetrasodium Pyrophosphate	Na ₄ P ₂ O ₇	52	71
Trisodium Phosphate	Na ₃ PO ₄ • H ₂ O	39	53
Trisodium Phosphate	Na ₃ PO ₄ • 12 H ₂ O	18	25
Tetra potassium Pyrophosphate	K ₄ P ₂ O ₇ • 3 H ₂ O	36.9	59

Phosphate Calculations Based On Orthophosphate Content

- PPM DSP in Feed water = $Ca + [(PO_4 \times 1.5)/C]$
- DSP = Disodium Phosphate
- Ca = Calcium in the Feed Water, ppm CaCO₃
- PO₄ = Phosphate residual in the boiler
- C = Cycles of Feed Water Concentration
- If you use Sodium Tripolyphosphate, use a multiplier of 0.83
- If you use Sodium Hexametaphosphate, use a multiplier of 0.72

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Phosphate Reactions High Pressure

- Except in High Pressure Boilers:
 - Congruent & Coordinated Phosphate programs are designed to treat high quality boiler water so that **Free Hydroxyl Formation is Prevented.**
 - Phosphate is used in Coordinated program as the pH buffer to limit localized concentration of Hydroxyl ions.
 - Disodium phosphate is fed to the boiler which reacts with any free hydroxyl ions to form trisodium phosphate. Which is less soluble.
 - Where bicarbonate alkalinity is present, use a molar ratio of 3 moles of sodium for every mole of phosphate to prevent break down of carbonate into carbon dioxide and hydroxyl ions.

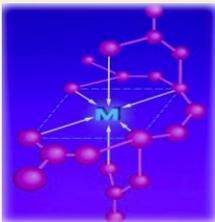
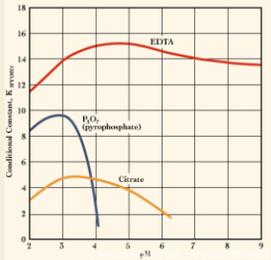
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Chelant Chemistry For The Prevention of Scale

HARDNESS + CHELANT = SOLUBLE SALTS

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Chelate Reactivity

The graph shows the Conditional Constant K' (y-axis, 0 to 18) versus pH (x-axis, 2 to 9). EDTA (red line) has the highest K' , peaking at approximately 14.5 around pH 5.5. P₂O₅ (diphosphate) (blue line) peaks at approximately 10 around pH 4. Citrate (orange line) peaks at approximately 5 around pH 5.5.

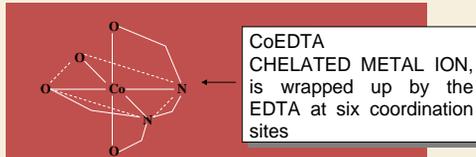


EDTA Ethylenediaminetetraacetic Acid

- ◆ The molecules or ions that surround a metal ion in the complex are called *ligands* (this is from the Latin word *ligare*, which means, "to bind")
- ◆ The atom in the ligand that is bound directly to the metal ion is called the *donor atom*.
- ◆ EDTA is a *polydentate ligand* ("many toothed") because it appears to grasp the metal ion between two or more donor atoms. *Polydentate ligands* as EDTA are therefore complexing agents, which surround the metal ion in an effect similar to a *crab claw*. Chelant comes from the Latin *chele*, which means to "claw"

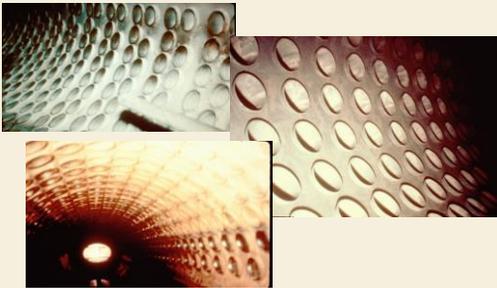


EDTA Complex Ethylenediaminetetraacetic Acid





Chelant (EDTA) Treated Boilers





There Is Always A Down Side



•EDTA is exceptional for preventing calcium scale formation.

•However, once all of the calcium and magnesium have been chelated (EDTA), then any excess chelant will seek other metals for reaction. In the boiler, it is iron.

•Therefore, an over feed of EDTA can result in metal loss.

•Chelant attack is seen as a gouging of the metal.



Chelant Calculations

- EDTA when expressed in these calculations is EDTA as a 38% solution. This is the commonly used strength of EDTA in the water treatment industry.
- Measure feed water cations (Ca, Mg, Fe) and multiply the chelant demand factor by 0.8. This is 80% OF THE REQUIRED CHELANT.
- This method allows most of the potential scale forming agents to be tied up in the chelant, but prevents chelant attack in the boiler.



Chelant Calculations EDTA Requirement Factors

Specific Factors to Cations

- Ca X 10.59 Mg X 8.69
- Fe +2 X 14.33 Fe +3 X 25.1

Factors for Calculation of Chelant Program

- **CDTH = FW TH, ppm CaCO3 x factor of 10**
- **CDFe = FW iron, ppm Fe x factor of 17.9**
- **CDCu = FW copper, ppm Cu x factor of 15.7**
- **BWchelant residual = BW chelant residual (1-3 ppm)**
- **CD = Chelant Demand**

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EDTA Program

- EDTA is fed to control 1 – 3 ppm as free EDTA, maximum.
- This is difficult to test for in the field, so most EDTA programs are fed based on a calculated feed rate
 - Determine Feed Water cations.
 - Use multipliers supplied for each cation
 - Total cation demand and multiply by 0.8
 - Use hardness test to determine if you have over fed EDTA to the boiler. Blue shows excess chelant feed.
 - Feed Sulfonated copolymer or terpolmer as dispersant

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EDTA REACTIONS

- The reactivity of EDTA on metal ions follows this reaction sequence;
- $Fe_{+3} > Cu > Fe_{+2} > Ca > Mg$
- Note: as a free ion, Ferric (Fe +3) ion reacts with EDTA first, then Copper, then Ferrous (Fe+2), followed by Calcium and Magnesium

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Chelant (EDTA) Clean Up

- You have a deposit in a boiler that is primarily tricalcium phosphate with some iron and silica. How do you do a Chelant clean up on this boiler?
- Do you run 10 - 30, 20 - 60 or 60 - 100 ppm of free EDTA in the boiler?
- Do you add phosphate to the boiler?
- Do you test phosphate in the boiler?
- What should the sulfite level be in the boiler?
- What is the proper feed point for the EDTA?
- How long do you run the clean up program?

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Chelant Clean Up - Procedure

Chelant clean up on a scaled boiler:

- Start at 10 – 30, then increase feed as required.
- Never add Phosphate during chelant clean up.
- You run a phosphate test to determine how fast the deposit is being removed. (1-4 ppm PO₄)
- Sulfite must be min. 30 ppm (chelant reacts to with oxygen when it is present)
- EDTA is fed to the feed water line 5' up stream from an elbow with a SS quill
- The clean up program is run until the boiler is clean

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Chelant Feed

The diagram illustrates the chelant feed process in a boiler system. It shows a Deaerator connected to a Boiler. Makeup water enters the Deaerator, which also receives steam and vent. Return condensate is fed back into the Deaerator. The Deaerator feeds into the Boiler. A Heat Exchange unit is connected to the Boiler. Chemical feed is added to the Boiler. A yellow arrow points to the 'Proper Feed point' for chelant, with a note: 'Feed either place and get chelant attack'.

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EDTA Vs NTA

- NTA
 - NITRILOTRIACETIC ACID
- FOUR COORDINATION SITES
- DOES NOT FORM AS SOLUBLE A COMPLEX AS EDTA
- UNUSED SITES ARE SUSCEPTIBLE TO REACTIONS WITH COMPETING ANIONS

- EDTA
 - ETHYLENEDIAMINETETRAACETIC ACID
- SIX COORDINATION SITES
- FORMS A SOLUBLE COMPLEX WITH CATIONS
- HIGH FEED RATE WILL REMOVE MAGNETITE BY COMBINING WITH THE FeO (FERROUS) PORTION OF THE MAGNETITE
- FORGIVING TREATMENT

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Chelant/Phosphate Products

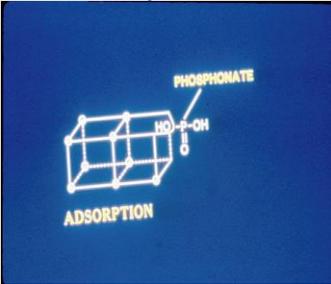
- Chelant (EDTA) and orthophosphate donors are combined in a product with dispersants for the prevention of scale
- Orthophosphate is easy to test for while chelants are difficult to test for in the field.
- Blend product to achieve desired chelant level where the phosphate residual is 5-15 ppm.
- Phosphate ions buffer EDTA, preventing aggressive attack on boiler metal
- Phosphate does not become a primary precipitant until there is a 20 ppm residual, so the chelant in this product is the primary scale control agent.

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PHOSPHONATES

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Adsorption Of Solid Vs Dispersion



Products as Phosphonates (HEDP & AMP) when used in boiler water treatment adsorb the solid into the Phosphonate molecule.

This reaction is similar to chelation, in that it removes the solid crystal from forming deposits

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Phosphonates – Sequester and Disperse

- Phosphonates are also used in boiler water treatment to assist in the prevention of deposits.
- Phosphonates sequester crystals of insoluble salts. This is usually accomplished by the adsorption of the metal ion onto the surface of the phosphonate, although it can include the function of sequestration.
- Used in combination with crystal modifiers, deposit forming salts can be both modified and partially solubilized.
- HEDP is the most commonly used Phosphonate for boiler water treatment, due to it's acceptance in food applications.**

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Phosphonates

- Phosphonates ability to remain stable in the presence of oxidation is improved, the fewer the phosphorus groups in the molecule.
- Addition of carboxyl groups to the molecule improve the dispersing ability of the molecule.
- HPAA is one of the few phosphonates that can use iron as it's functional metal.

CN(C)C(=O)OP(=O)(O)O ATMP

OP(=O)(O)C(COP(=O)(O)O)C(=O)O HEDP

CC(=O)OP(=O)(O)C(C(=O)O)C(=O)O PBTC

CC(=O)OP(=O)(O)C(C(=O)O)O HPAA

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Phosphonates & Boiler Water Treatment

- Tested at 25°C, 600 psi, 40 - 100 ppm as material, 500 ppm Sodium Sulfite in an autoclave.
- ATMP [50% Aminotri(methylene phosphonic acid)] 9.33 days to completely break down.**
- HEDP [60% 1-Hydroxy-ethylidene 1,1-diphosphonic acid] 4.5 days to completely break down**
- Percentage of Decomposition**
 - ATMP 1.3% @ 6 hrs 2.6% @ 12 hrs 5.3% @ 24 hrs
 - HEDP 2.8% @ 6 hrs 5.6% @ 12 hrs 11.1% @ 24 hrs
- HEDP is the only FDA approved phosphonic acid for use in boilers.
- ATMP will attack the cobalt sulfate, removing the catalyst. Therefore, do not add ATMP product and catalyzed sodium sulfite together in the feed water unless you are looking forward to oxygen pitting.

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DISPERSANTS

POLYMER TECHNOLOGY

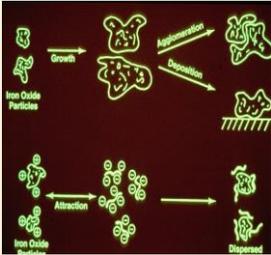
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Dispersants Make It Slick So it Don't Stick

- When a salt in water is no longer soluble in water, it has reached the threshold level, where that solid drops out and forms a deposit.
- At this point, **nucleation**, or the formation of crystals at a submicroscopic level begins. Uninhibited, **nucleation** allows deposits to form and build up as the crystals grow.
- Dispersants use **polyanions**, negatively charged long chain polymers, to disrupt this nucleation.
- Polyanions attack the crystal at the cationic sites (Calcium, Magnesium, Iron, Strontium, etc.). This interrupts the formation of the crystal growth. Which prevents the growth of the crystal in the boiler water.
- **All positive charges are then neutralized by the polyanion, creating a colloidal that is now electronegative. The particles are now self repelling. Makes it slick so it don't stick.**
- **THRESHOLD TREATMENT**

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Dispersion - Agglomeration



Agglomeration occurs as the solids in the boiler become concentrated and precipitate out of the system.

They tend to build in layers on heated surfaces and the bottom of the boiler.

The key to dispersion is to interrupt the Agglomeration (building of the solids) and then to repel each particle from the other using **polyanions**

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Molecular Weight

- Polyanions cause disruption in crystal growth, so particle size becomes important.
- *The particle is colloidal, so the molecular weight of the polyanion will determine the size of the particle.*
- For waste water, we want a high molecular weight. In For boiler water, the dispersant is usually below 10,000 MW
- Rules of Thumb for M_w
 - <5,000 Threshold Inhibition
 - >5,000 Dispersion
 - $\sim 10^6$ Coagulation
 - $\sim 10^7$ Flocculation

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Functionality of Polymers

- Threshold Inhibition
- Chelation
- Stabilization
- Crystal Habit Modification
- Particulate Dispersion

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Definition – Threshold Inhibition

- Threshold Inhibition is defined as maintaining a solubility of an otherwise insoluble salt beyond it's saturation limits using an additive at **sub-stoichiometric** levels.
- *Threshold Inhibition is generally viewed as a temporary effect.*
- Duration of Inhibition is related to:
 - Driving force for precipitation
 - Efficacy of Inhibitor
 - Water Impurities (both dissolved and suspended)
 - Frequency of Additive Dosage

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Definition – Driving Force

- Driving Force for Mineral Scale Precipitation is a general term used to refer to the severity of conditions (pH, temperature, precipitating ion concentrations, contamination, corrosion, evaporation.....) that contribute of precipitation tendency of a given compound.
- This is not a specific term, it is a suggestion of degree or potential for the formation of scale.

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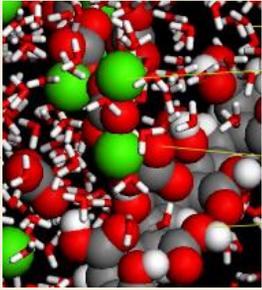
Definition – Chelation Vs Polymers

- A Chelate is a coordination compound in which a central metal ion such as Fe^{2+} is attached by coordinate links to two or more non-metal atoms in the same molecule, called ligands – Condensed Chemical Dictionary
- Polymers act as chelates with most multi-valent ions due to their multiple binding sites.
- Basically, the term **chelate** tends to imply a more **permanent** or substantive combination between the ion and the ligand (i.e. EDTA)
- **Polymers**, of the type we use in water treatment, do not meet the common definition of a chelant as their association is generally **temporary**.

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Polymers – Metals Attraction

CC(=O)O
 acrylic acid
 $n=28, 70, \dots$



Water

Calcium-ion

Carbonate-ion

Poly-acrylate

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Definition - Stabilization

- Can have two meanings with respect to polymer interactions with metal ions:
 - Colloidal – Precipitation occurs but polymer prevents agglomeration of particles beyond 1 micron in size. These particles are thus stabilized via electrostatic interactions with the polymer.
 - Typically are not visible (exception iron)
 - Stabilization can fail due to physical or chemical changes in the fluid.
 - A synonym for sequestration where the coordination complex is typically referred to prevention of precipitation. This is a stoichiometric relationship.

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Dispersing Agents and Crystal Distortion

- Most of the dispersants that are used in boiler water treatment are crystal distorting products.
- Maleic distorts the calcium carbonate crystal structure so that it is less adherent.
- Consider calcium carbonate as a square box covered with Velcro. It stacks tight. Crystal distortion squashes the box, rips off the Velcro and lubricates the edges.
- Phosphate is usually dispersed with a low molecular weight (2500 - 5000 MW) Polyacrylate or Polymethacrylate.
- Maleic is used for distortion and dispersion of calcium carbonate
- Styrenated copolymer are used for dispersion of iron in the boiler.
- Copolymers and terpolymers combine the abilities of two or more different types of dispersants

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Definition - Crystal Habit Modification

- Crystal Habit is generally defined as the normal size and shape of a precipitated substance in a given set of environmental conditions.
- Crystal growth is dynamic. Crystalloids that do not grow tend to redissolve.
- Polymers and other materials such as phosphonates can modify the size and shape of mineral crystal habits.
 - $\text{CaCO}_3 > \text{Ca}_3(\text{PO}_4)_2, \text{BaSO}_4 \gg \text{CaSO}_4$
- Crystal Habit Modification is the basis for scale control using polymers
 - Threshold Inhibition
 - Deposition Tendency
 - Surface Adherence

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Crystal Habit Modification

- Unstable crystals tend to re-dissolve, and therefore do not "stick" or form scale on metal surfaces.
- Crystal modification is an extension of threshold stabilization. Both involve adsorption of specific molecules on a growing crystal lattice.
- Chemicals that show good threshold inhibition are typically good crystal modifiers.

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Proposed Crystal Modification Mechanism

Drinking Water Treatment Handbook

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Crystal Modification - Dispersant

Maleic copolymer interferes with the crystal growth of Calcium Carbonate.

The result is irregular crystal growth and a reduction in the ionic intercrystal attraction.

Scale formation potential is reduced.

Crystal distortion, poor dispersion – Maleics are crystal distorting compounds – Crystal Habitat Modifiers

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Acrylamido-Methyl Propane Sulfonate - AMPS

- **AMPS**
- **Acrylamido-methyl-propane sulfonate**
- **Most effective polymer for phosphate scale control.**
- **Good for calcium carbonate and calcium phosphate scale inhibition.**
- **Affinity for control of iron in the boiler water (sulfone group)**

$$\left[\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{C}=\text{O} \end{array} \right]_n$$

$$\left[\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{C}=\text{O} \\ | \\ \text{N} \\ | \\ \text{R}' \quad \text{R}'' \end{array} \right]_p$$

Where
R' and R'' = H or -CH₃ or -C₆H₅

$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\ | \quad | \quad | \\ \text{H} \quad \text{H} \quad \text{H} \\ | \\ \text{O}-\text{S}=\text{O} \\ | \\ \text{O}^- \\ | \\ \text{Na}^+ \end{array}$$

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Acrylic Acid/Acrylamido – Methyl-Propane Sulfonate AA/AMPS

- **AA/AMPS**
- **Acrylic Acid/Acrylamido-methyl-propane sulfonate**
- **Due to including carboxyl group (Acrylic), very high tolerance for calcium salts.**
- **Good tolerance for zinc compounds.**
- **Strong polarity due to sulfonic acid group**

$$\left[\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \quad \text{COOH} \end{array} \right]_n$$

$$\left[\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{O}=\text{C} \quad \text{CH}_3 \\ | \\ \text{NH}-\text{C}-\text{CH}_2\text{SO}_3\text{H} \\ | \\ \text{CH}_3 \end{array} \right]_m$$

$$\left[\begin{array}{c} \text{H}_2\text{C} \\ | \\ -\text{C}-\text{CH}- \\ | \quad | \\ \text{O}=\text{C} \quad \text{OH} \end{array} \right]_m$$

$$\left[\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{O}=\text{C} \quad \text{CH}_3 \\ | \\ \text{NH}-\text{C}-\text{CH}_2\text{SO}_3\text{H} \\ | \\ \text{CH}_3 \end{array} \right]_n$$

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Phosphonocarboxylic Acid

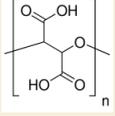
$\text{HO}-\text{C}=\text{O}$
 PH_2

- **PCA**
- **Phosphonocarboxylic Acid**
- **High pH, High Alkalinity, High Hardness, High Temperature.**
- **Strong Chlorine Tolerance.**
- **Very stable with high dispersant capabilities on calcium, barium and strontium salts**
- **Both phosphonate (adsorption) and carboxyl (dispersancy) capabilities.**
- **Effective when blended with Maleics (crystal distortion) and Sulfones (iron control).**

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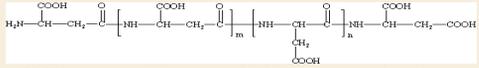
Polyepoxysuccinic Acid - PESA

- PESA is a scale and corrosion inhibitor that does not contain either phosphorus or nitrogen (GREEN TECHNOLOGY).
- PESA has good scale inhibition and dispersion for calcium carbonate, calcium sulfate, calcium fluoride and silica scale. It is effective in high hardness, alkalinity and pH.
- It has superior calcium salt scale control when compared to phosphonates and acrylates.
- PESA is biodegradable
- PESA is very effective in high scaling conditions
- PESA is used in cooling and boiler water applications.
- Thermally stable up to 330°C
- PESA is stable in the presence of oxidizers as chlorine



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Polyaspartic Acid (PASP)



- **PASP** is a water soluble, green technology dispersant, that does not contain phosphorus and is fully biodegradable. (NON-POLLUTING)
- **PASP** is a strong chelating agent for calcium ions. It is an antiscalant for calcium carbonate, calcium sulfate, barium sulfate, calcium phosphate, etc.
- **PASP** displays both dispersion and corrosion inhibitor properties.
- **PASP application scope and application method:**
 - Used for scale and corrosion inhibition in; cool water system, boiler water and reverse osmosis, where the water has high hardness, alkalinity and pH.
 - Blend with PBTC to improve the performance of both for scale control.
 - It is used in agriculture for nutrient absorption, to improve the production of vegetable, fruit, and flowers. (GREEN TECHNOLOGY)

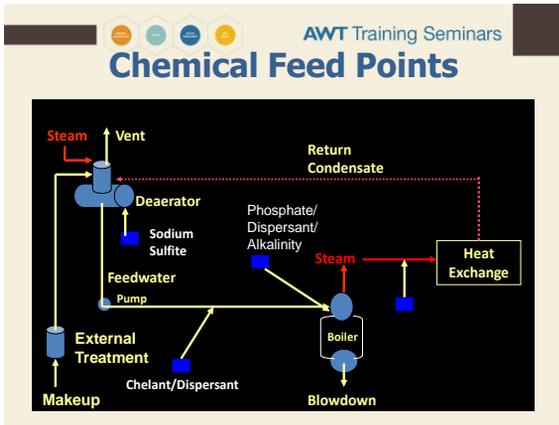
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Dispersant Reactivity

- There are many different types of dispersing agents.
 - Acrylates, Maleic, Copolymers, AMPS Copolymers, and Terpolymers.
 - Each polymer is designed to attack crystalline growth in a different way. Each polymer is designed to cause a phase change in the ionic charge of the particles to cause dispersion.
- These polyanions do not discriminate when it comes to reaction. Some are more specific to a type of insoluble salt, but in general, they all will react with cations in the system.
- Polymer activity is dependent on Hydroxyl ion (OH-) availability
- General rule of thumb is to feed 30 – 45 ppm as polymer

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Polymer	Name	Comments
PAA	Polyacrylic Acid	CaCO ₃ , Ca ₃ (PO ₄) ₂ , CaSO ₄ microcrystal dispersant. Good in high alkalinity, not recommended for sediment
HPMA	Polymaleic	Low molecular weight, poor dispersant, good crystal modification. Thermally stable to 330°C. Nontoxic, good on carbonates and phosphates
MA/AA	Maleic/ Acrylic Acid Copolymer	Thermal stability 300°C with distortion ability of Maleic, coupled with the carbonate dispersancy of PAA. Good for carbonates and phosphates.
AMPS	Acrylamido-methyl-propane sulfonate	Most effective polymer for phosphate scale control. Good for calcium carbonate scale inhibition
AA/AMPS	Acrylic Acid/ Acrylamido-methyl-propane sulfonate	Due to including carboxyl group, very high tolerance for calcium salts, good tolerance for zinc compounds. Strong polarity due to sulfonic acid group
PCA	Phosphonocarboxylic Acid	High pH, High Alkalinity, High Hardness, High Temperature. Strong Chlorine Tolerance. Very stable with high dispersant capabilities on calcium, barium and strontium salts



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Alkalinity

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Carbonate & Bicarbonate Alkalinity

- The Alkalinity in most natural water supplies is caused by dissolved bicarbonate (HCO₃).
- **CARBONATE (CO₃) / BICARBONATE (HCO₃) DISTRIBUTION**
- Most natural waters with a pH that is less than 8.2-8.4 contain alkalinity as bicarbonate. Above this pH, the CO₂ in the water is dramatically reduced and the alkalinity is found as carbonate alkalinity.
- **HCO₃ ↔ CO₃ + H**

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Carbonate & Bicarbonate Alkalinity

- In the pH range between 8.2 – 9.6, which is considered above the P. Alkalinity end point, Bicarbonate and Carbonate ions exist together in the absence of measurable Carbon Dioxide or Hydroxyl ions.
- As the pH of the water increases above a pH of 9.6, the Hydroxyl Alkalinity becomes measurable.
- Where you have evolution of Hydroxyl ion and the M. Alkalinity is greater than the P. Alkalinity, the distribution between the Carbonate and the Hydroxyl can be calculated as:
 $CO_3 = 2(M - P)$ $OH = 2P - M$ $HCO_3 = 0$

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Alkalinity Relationships

Ions	$P = 0$	$P < M/2$	$P = M/2$	$P > M/2$	$P = M$
(OH)	0	0	0	$2P - M$	M
CO₃	0	2P	M	$2(M - P)$	0
HCO₃	M	$M - 2P$	0	0	0

Bicarbonates + hydroxides do not exist together
 CO₂ does not exist with carbonates

"P" Alkalinity = 1/2 carbonates and all hydroxides
"M" Alkalinity = all hydroxides, carbonates and bicarbonates



Importance of Boiler Alkalinity

- Alkalinity contributes the Hydroxyl ion (OH-) that is required for the formation of magnetite, a protective film on the boiler tubes.
- Alkalinity contributes the Hydroxyl ion (OH-) that is needed for the proper phosphate reactions
- Alkalinity enhances dispersant reaction by making solids particles smaller with less charge (metals in the presence of (OH-) form a small particle which is an insoluble hydroxyl state of the metal.



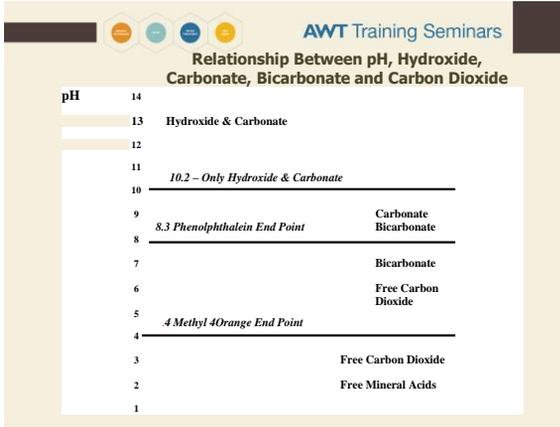
Alkalinity Can Cause Carry Over

- As the alkalinity in the boiler increases, the viscosity of the boiler water increases. This in turn increases the surface tension on the surface of the boiler water.
- Hence, once the surface tension becomes too high, steam that is exiting the boiler will pull water with it. This results in surging and eventually carryover of boiler water.
- Carry over pulls water out of the boiler into the steam line.



Carry Over

- Carry over causes the following problems:
 - Contamination of steam, which in turn contaminates product.
 - Low water in the boiler during carry over can shut down the boiler
 - Sudden and frequent carry over will cause deposit formation on exposed tubes and can result in tube failure from over heating.
 - Alkaline boiler water in the condensate can dissolve copper components in the system
- Carry over can be caused by faulty water level controls. If water level control does not keep up with the water requirement in the boiler, the water expands and bubbles form, causing carry over



END DAY 1

Condensate Contamination

Oxygen
Carbon Dioxide
Other Contaminants

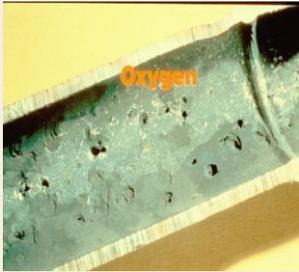


Condensate

- Condensate is extremely valuable.
 - Pure condensate is already heated and it has no solids.
 - An increase in condensate return percentage is a reduction in make up water requirement
 - An increase in condensate return percentage is a reduction in blow down, chemical usage requirement and fuel consumption.
 - Condensate contamination can negate all of these benefits.
 - It is the water treaters job to keep the condensate as pure as possible.



Oxygen Pitting Contamination



- When Oxygen enters the condensate return system, it will cause pitting on the top of the condensate return line.
- Oxygen can enter the system through vacuum breakers that are placed in the heating systems or on long runs to prevent water hammering.
- Oxygen can enter the system through open condensate receivers.



Carbon Dioxide Contamination



- Carbon Dioxide is formed in the boiler from the break down of carbonate (CO_3).
- In that CO_2 is a highly volatile gas, it leaves the boiler with the steam.
- The higher the raw water (make up) total alkalinity, the greater the amount of carbonate and hence, the higher the level of CO_2 in the steam.

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Carbon Dioxide Becomes Carbonic Acid



- Carbonic acid is formed by bubbling carbon dioxide through hot water.
- As the steam is condensed in the trap, the carbon dioxide in the steam is bubbled through this hot condensate.
- The result is the formation of carbonic acid.
- The amount of total alkalinity in the raw water determines the amount of carbonic acid that is formed in the condensate system.

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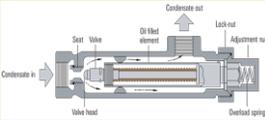
Basic Trap Designs

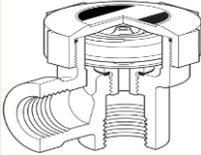
- Steam Traps are used to allow the steam to condensate and then be released as condensate to the return system. Some of the most common types are;
 - Thermostatic
 - Bi-Metal
 - Disc
 - Float
 - Inverted Bucket

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Liquid Thermostatic Traps

- Trap has liquid that is heated as it contacts steam. This expands the liquid closing the trap.
- As the steam cools to condensate, the trap liquid also cools.
- Once cooled, the trap liquid contracts, releasing the condensate and then exposing itself to the steam

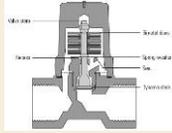






Bimetallic Trap

- Trap has high expansion and low expansion metal.
- Steam causes the high expansion metal to expand and close the trap
- Cooled condensate gradually contracts the metal and the trap opens





Thermodynamic Disc Trap

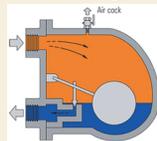
- Steam enters the trap and forces itself into the bottom chamber.
- Condensate is formed and the pressure of the condensate lifts the disk
- This allows the condensate to leave the trap.
- Disk closes as the condensate pressure is relieved





Float & Thermostatic Trap

- Steam enters the trap, driving the ball down.
- As condensate accumulates, the ball rises opening port to allow condensate to release.
- Minor steam loss if vented. Venting also allows this valve to modulate
- Cold vented trap could pull in air with potential oxygen pitting.



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Inverted Bucket Trap

The diagram illustrates the operation of an inverted bucket trap. It shows a cross-section of the trap with an inverted bucket inside. The bucket is held in place by a float valve. When the bucket is full of condensate, the float valve is closed, preventing steam from passing. When the bucket is empty, the float valve opens, allowing condensate to drain. The diagram also shows a bleed hole that allows air and steam to pass through when the bucket is open, preventing a vacuum from forming.

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Carbonic Acid Attack

- Carbonic acid once formed, reduces the pH of the condensate.
- This acidic condensate then gradually eats away at the bottom of the condensate line, until the metal becomes thin enough for it to leak. This usually occurs first at the threaded section of the line.
- Besides destroying the condensate return piping, carbonic acid attack will bring iron back to the feed water system and to the boiler.
- This iron will cause increased corrosion, form deposits, eat up any chelant in the boiler and interfere with the dispersant program

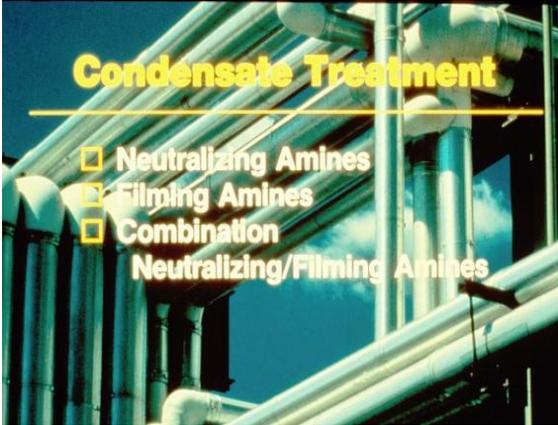
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WATER LEAK REFERENCE TABLE

LEAK THIS SIZE	LOSS PER DAY* (GALLONS)	LOSS PER YEAR* (MILLION GALLONS)
• 1/16"	989 (3,215)	0.35 (0.48)
• 1/8"	3,972 (5,380)	1.5 (1.9)
• 1/4"	15,900 (21,280)	5.8 (7.7)
• 3/8"	35,900 (47,800)	13.1 (17.5)
• 1/2"	63,800 (85,000)	23.3 (31.6)
• 5/8"	99,600 (132,800)	36.4 (48.5)
• 3/4"	143,400 (191,200)	52.3 (69.8)
• 1"	255,800 (340,000)	93.1 (124.1)

* BASED UPON 66 (88) PSI

Condensate Corrosion Losses Due to Leak Size



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Neutralizing Amines

- Neutralizing amines are used to control carbonic acid corrosion.
- The concept is that by using volatile alkaline amines, you neutralize the carbonic acid as it is formed. By maintaining a slightly alkaline pH in the condensate return system, you prevent carbonic acid attack.
- A pH between 7.6 - 8.8 is usually effective for the prevention of carbonic acid attack.
- Neutralizing amines can be fed to the boiler. This feed method will allow the majority of the amine will evolve out of the boiler with the steam.
- The most effective feed point is via a stainless steel injection quill directly into the steam header.

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Neutralizing Amines Selection

- The down side of using neutralizing amines is that the different types of neutralizing amines have different distribution ratios.
- A neutralizing amine's distribution ratio determines how long the neutralizing amine will carry in the steam.
- A low distribution ratio means that the neutralizing amine will drop out early and not protect the longer runs in the system. A high distribution ratio, means that the neutralizing amine will carry for a long distance, but that it will not protect a short run.


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Neutralizing Amine Distribution Ratio Based on Pressure

Amine	MW	Neutralizing Capacity (ppm CO2/ppm amine)	Ratio 0 psi	Ratio 200 psi	Ratio 1000 p
Ammonia	35	2.59	10	7.14	3.57
Cyclohexylamine	99	0.444	4	23.3	9.3
Diethylaminoethanol	117	0.376	1.7	4.5	3.4
Methoxypropylamine	89	0.494	1	2.4	2.5
Morpholine	87	0.506	6.4	1.6	0.98
Diethanolamine	105	0.419	0.004	0.11	0.07


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Neutralizing Amine Characteristics

	Morpholine	CHA	DEAE	AMP	DEHA	MOPA
Boiling Point 100% Amine	264°F	273°F	325°F	329°F	257°F	245°F
Boiling Point (Amine/Water)	Nonazeotrope	Azeotrope 203°F	Azeotrope 219°F	Nonazeotrope	Nonazeotrope	Nonazeotrope
Decomposition Temperature	644°F	626°F	794°F	680°F	560°F	
Liquid Vapor Distribution Ratio	0.4:1	4.7:1	1.7:1	0.3:1	1.3:1	1.1 – 1.4:1
Comments	Min 48 psia Short runs	Low Pressure Long runs	Med. To Long runs	Min 75 psi Short to med. runs	Med. To Long Runs	Med. To long runs
Pressure Reduction Cross Over	Not below 35 psia	Yes	Yes	Not below 75 psi	Minimal below 30 psia	Minimal below 30 psia


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Blending Neutralizing Amines

- In that condensate return systems have some short runs, some long runs and some medium runs, it is common practice to blend two or three of the neutralizing amines together to form a product that is able to protect all of the system.
- In FDA regulated plants you are restricted in the amount of amine that you can put into a system.
 - CFR 21 173.310 states 15 ppm of DEAE, 10 ppm of Cyclohexylamine, 10 ppm of Morpholine.
 - Hence blends are usually 3 parts DEAE, 2 Parts Cyclohexylamine or 3:2:2 of Diethylaminoethanol/Cyclohexylamine/Morpholine
 - Amine total is to be maximum of 25 ppm

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DEHA

- Where the steam does not contact food, DEHA should be considered in conjunction with the neutralizing amine.
- DEHA will act as a strong reducing agent in the boiler, controlling oxygen, it will then carry out of the boiler in that it is a volatile amine.
- Once in the steam system, DEHA will reduce iron. This reaction forms a protective magnetite film on the pipe.
- DEHA can be blended with any of the neutralizing amines.
- DEHA/neutralizing amine blends are used to push DEHA out into the system, where it will reduce corrosion and assist in controlling periodic oxygen intrusion.

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DEHA

- Coupon on the right was in a condensate line that had oxygen present.
- Coupon on the left was treated with DEHA in the same system. Reverted corrosion to black magnetite.



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Where Neutralizing Amines Can't Do It All



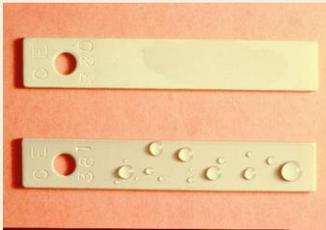


WHY Use A Filming Amine Instead Of Neutralizing Amines?

- Oxygen - Neutralizing amines have no effect on oxygen
- Economics - In highly alkaline water, the cost of using a neutralizing amine may be excessive. In this case, a cost comparison may show that it is much less expensive to use filming amines over neutralizing amines.



Filming Amines



•Filming amines are aliphatic hydrocarbon based materials that protect the condensate system by laying down a film on the metal surface.

•This film protects the metal from corrosion by preventing carbonic acid and oxygen from contacting the metal surfaces



Filming Amines - ODA

- Primary amine is ODA (Octadecylamine). This product will attach to metal surfaces with one hydrophobic end. Hence, over feed of the product can result in a build up that will plug a condensate return line.
- Since ODA attaches to the metal surface, any corrosion byproducts that are present will be lifted off. Once lifted, these iron particles travel down line and can plug up strainers and lines.
- ODA is fed to the system based on steam production, the total alkalinity of the make up water is not a consideration for determining feed rate.



Filming Amines – ODA Feed

- To prevent shutting down the condensate system when you start feeding ODA, initially feed only 25% of the calculated feed rate for the first two weeks to a month. Then go to 50% for two weeks, 75% for the next two weeks and then to 100%. If the system is old and fouled, extend the time between increases in the feed rate
- Filming amines are fed to the steam header only. In that they are only partially volatile, feeding a filming amine to the boiler will result in the majority of the product staying in the boiler.



Tertiary Amine

- Tertiary amines have three hydrophobic sites.
- They attach almost horizontally. Therefore, they do not tend to build up and plug lines the way primary amines do.
- Tertiary amine have a much lower viscosity than primary amines, so they can easily be blended with neutralizing amines.
- Tertiary amines are generally derivatives of soy bean or tallow oils.
- Tertiary amines are to be fed to the steam header.
- Tertiary amine feed should be started in a system in the same manner as the primary amine feed.



Blending Filming And Neutralizing Amines

- Filming amines function better in a pH range that is slightly acidic (6.5 - 7.5), so, why blend a neutralizing amine with a filming amine?
- Neutralizing amines will thin the filming amine film, thus spreading the film farther and reducing the potential for line blockage.
- Neutralizing amine/Filming amine blends are used to run a low pH system (7.2- 7.8) where there is a low oxygen contamination threat and yet the carbonic acid potential is also low.

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PHOSPHATE PROGRAM

- CONTROL LIMITS
 - > 20 – 60 PPM PO₄
 - > 250 – 800 PPM OH ALK
 - > 30 – 60 PPM @ SULFITE
 - > 7.8-8.8 PH CONDENSATE
 - > CONDUCTIVITY
- DISPERSANT LEVEL?
- WHAT ARE THE COMMON PROBLEMS?
- PRODUCTS
 - SODIUM HEXAMETAPHOSPHATE
 - SODIUM HYDROXIDE
 - AA/AMPS/SA COPOLYMER
 - POLYACRYLATE
 - SODIUM SULFITE
 - NEUTRALIZING AMINE

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CHELANT/PHOSPHATE PROGRAM

- CONTROL LIMITS
 - PO₄ 5 – 15 PPM
 - 3.5% SHMP
 - 10% EDTA
 - 14% DISPERSANTS
- OXYGEN SCAVENGER
- PH 7.8 – 8.8
- CONDUCTIVITY
- PRODUCT
 - EDTA
 - SHMP
 - AA/AMPS/SA
 - HPMA/PAA/PCA/AA-SA
- OXYGEN SCAVENGER
- RETURN LINE TREATMENT

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CHELANT PROGRAM

- EDTA TO 80% OF DEMAND
- DISPERSANT BASED ON LOADING
- OXYGEN SCAVENGER
- INSPECT FOR EDTA CORROSION
- FEED TO FW LINE
- TEST FEED WATER
- EDTA
- DISPERSANT
 - AA/AMPS/SA
 - PCA
 - HPMA
 - PAA
- OXYGEN SCAVENGER
- RETURN LINE TREATMENT

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ALL ORGANIC - DISPERSANT

- ALKALINITY FROM SOFT WATER AND AUGMENTED HYDROXIDE FEED.
- OXYGEN SCAVENGER
- DISPERSANT
 - AA/AMPS/SA
 - HPMA
 - AA/SA
 - PAA
 - PCA
- ALKALINITY
- OXYGEN SCAVENGER
- RETURN LINE TREATMENT
- DISPERSANT FEED
 - WATER METER PACED
 - TRACED POLYMER
 - CARBOXYL TEST
 - FLOURESCENT DYE

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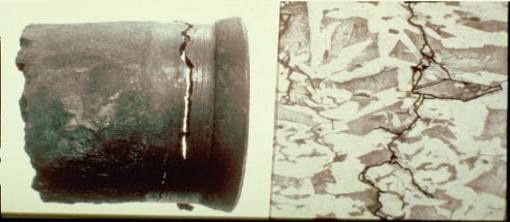
VOLATILE FILMING AMINE

- Initially feed 25% of recommended feed rate into the feed water.
 - Feed based on make up meter
 - Increase feed rate by 25% as water clears, until final level is obtained in the system
- Products are recommended to be fed at a rate of 1000 ppm of product into a system
 - Recommended control range is 800 – 1000 ppm as product.
 - Field study has found that 400 – 800 ppm as product is effective to clean a boiler
 - 600 ppm is effective as a maintenance dosage
- Measure in condensate and control 0.2 – 1 ppm using Rose Bengal Photometric Test

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FIELD DETERMINATION OF FAILURES

DEPOSITS
SCALES
METAL LOSS



The left image shows a dark, heavily corroded metal pipe with a jagged crack. The right image shows a cross-section of a pipe filled with white, crystalline scale deposits, with a network of cracks visible within the metal structure.



Field Deposit Determination Procedure

- Categorize the deposit in one of the following areas:
 - a. Scale
 - b. Sludge
 - c. Metal Oxide
 - d. Complex Sodium Metal Silicates
 - e. Organic (oil, lignin/tannin, dyes, etc.)



Scale Deposits

- Scale deposits will appear to be fairly smooth-surfaced to the eye, they will have a generally uniform coat on most of the waterside surfaces (heaviest at high temperature zones), and will generally be very hard and dense.
- The usual causes for the formation of a scale deposit are; no chemical or pretreatment equipment on the system and exceeding the solubility limits (insufficient blow down or excessively high chemical residuals).



Scale Deposits



Tricalcium Phosphate



Pipe Accumulation



General scale in mud drum



Sludge Deposition

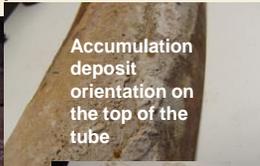
- Sludge deposits are not smooth-surfaced and will tend to have an irregular surface formation.
 - This can appear to the eye similar to a series of points or ridges.
 - They can be layered or formed from agglomerated masses.
 - Sludge deposits are generally found in low flow areas of the boiler, such as, top of tubes, bottom of the boiler, the tube ends at the rear of a water tube boiler.
- The usual causes for sludge deposits are; low alkalinity, insufficient dispersant usage, incorrect dispersant selection, insufficient blow down, or erratic control of any or all of these problem areas.



Sludge Deposition



Accumulated sludge from lack of blow down formed on top



Accumulation deposit orientation on the top of the tube



Agglomerated Calcium Carbonate



Metal Oxides

- Metal oxides are corrosion by-products, which will form a hard, dense, highly insulative deposit.
- They are formed when iron or copper levels are high and the dispersant level is low.
 - Once they are formed, they are difficult to remove.
 - The usual causes for this type of deposition are;
 - incoming iron in the feed water or corrosion by-products from the condensate.
 - Iron in the make up must be removed with iron removal equipment.
 - Iron or copper in the condensate needs to be stopped with the use of a properly designed amine product, or it needs to be dumped.

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Iron Deposits



The slide features four photographs illustrating iron deposits. Top left: A brown, crusty deposit on a surface. Middle left: A dark, irregular flake labeled 'Accumulated Iron Deposit'. Top right: A red pipe with a dark coating labeled 'Iron Deposit'. Bottom right: A pile of greenish-brown particles labeled 'Chips'.

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Complex Deposits

- Complex sodium metal silicates of sodium silicate, iron silicate or sodium aluminum are rare in the any large quantity in the boiler.
- Where they do occur, they are extremely hard and insulative.
- This deposit will cause rapid over heating of the boiler metal and tube failure.
- It is formed where silica is allowed to remain in excess of 180 ppm in the boiler water and where the alkalinity has remained low in the boiler water for an extended period of time.

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Organics

- Organics come from oil, lignin/tannin, unclarified surface water, and process contamination.
- Fouling is usually lumped in with the sludge deposits and is caused by the introduction of low quality water to the boiler.
- Organics will form a heavy sludge that impedes boiler circulation.
- The proper use of dispersants, increased blow down and maintaining in excess of 250 ppm as Hydroxyl Alkalinity can control this condition.



What Is In The Deposit?

- Most deposits are made up of more than one impurity.
- To correct the problem, you need to know what the deposit is made of.
- Once you know what the deposit is made of, you can determine what occurred in the system to allow it's formation. *by it was formed.*



Note the Appearance of the Deposit

- Scale deposits (calcium carbonate, calcium sulfate, and silica) have smooth surfaces, are hard and dense, coat all of the water surfaces and will be white to gray in color.
- Sludge deposits range from scale like deposits to agglomerated sludge masses with irregular surfaces.
 - A dispersant will suspend the sludge this results in a smoother uniform deposit, very similar to a scale.
 - The key to distinguishing the different type of deposit is the lower deposit density and periodic irregularities coupled with layering.
 - Sludge deposits are typically calcium phosphates, iron oxide based sludge, magnesium phosphate, magnesium hydroxide and magnesium silicate.



Analysis of Deposit

- Take a small piece of the deposit and place it in a flask.
 - Add concentrated Hydrochloric Acid to the deposit.
 - If a yellow color develops, iron is present.
 - If a green color develops, copper is present.
 - Strong effervescence (foam) indicates that carbonates are present. If strong effervescence occurs, note the sample size before and after the HCl was added. This can give a general idea as to what percentage of the deposit is carbonate based.



Sulfate & Sulfides

- Take another sample of the deposit and add a dilute HCl (1.0 Normal or less). If a rotten egg odor is noticed, sulfates or sulfides are present.
- Now, note the color of the sample of deposit.
 - If the sample was white before it went into the acid solution, the deposit probably contains calcium sulfate.
 - If the sample was black, the deposit is probably iron sulfide



Phosphate Deposit

- Add Nitric Acid to another deposit sample.
- Then add the Molybdate reagent from the phosphate test.
 - A blue color indicates the presence of phosphate.
 - Note; over feed of a phosphate in this case will usually create a white powdery deposit, while phosphate, complexes will be grayish.



Field Quantitative Analysis

- Take a fresh sample and crush it as best you can.
- Use 1 gram (approximately the size of the large spoon used for the acid starch reagent) of the sample and place it in concentrated Hydrochloric Acid.
- This could take a few hours. If over 75% of the sample dissolves, continue on.
- If the largest portion of the sample does not dissolve, then silicate complexes are present and a detailed lab analysis will have to be run.



Field Quantitative Cont.

- Note in the sample that was just dissolved, the tenacity of the deposit is determined by the length of time which was taken to dissolve the deposit.
- Filter the liquor from with #41 filter paper. Take 1 ml of this filtered liquor and add it to 99 ml of DI water.
- Test this solution with your test kit for; iron, magnesium hardness, calcium hardness, phosphate, sulfate and copper.
 - If the results are off the scale, dilute the sample again by putting 10 ml of the solution into 90 ml of DI water.
 - Now add the ppm results that were found and divide each test result by the total.
 - This will yield relative percentages to the constituents of the deposit. It will also determine the predominant compounds that make up the deposit.



Calcium Carbonate

- Deposit Appearance?
- Deposit Density?
- Removed from the tray section of the DA.
- Dissolved completely in HCl.
- What is it?
- Why did it Form?





Condensate Corrosion

- Coupon on the right was exposed to 30 days of condensate from a remote receiver.
- Coupon on the left was exposed to DEHA in the same line for 30 days.



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Condensate Line

- Make up water has high alkalinity.
- Product used is blend of DEAE and Cyclohexylamine
- Deposit was soft and gel like when wet, and is hard dry.
- What is it?



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- System had used a filming amine.
- Just started using neutralizing amine
- Maintained the pH of the condensate at 8.5 – 9.0 for the first 30 days that neutralizing amine was fed.
- Why a deposit?



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Corrosion or Pitting?

- Extensive metal loss where the tube meets the tube sheet
- Tube was closest to the fire tube in the hottest area.
- The rest of this tube and the other tubes have no sign of pitting
- Boiler used single probe level control.
- 80% condensate return:
- No condensate return:



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Corrosion

- Feed water tank leaked on the side about half way up.
- Cut shows top picture
- Chips in bottom picture were in the bottom of the tank
- Program used sodium sulfite and injects it into the boiler.



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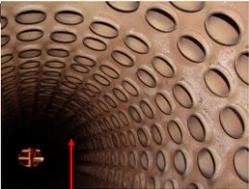
Erosion or Corrosion

- Copper line
- Line does not see chemical program
- Domestic hot water is in the line
- Line is located near the booster pump
- System flow rate has doubled over the last few months.



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Boiler Inspection




Idle Hospital Boiler – Phosphate/Dispersant Program

Fire tube boiler in plastic extrusion plant

Steam Drum in Pharmaceutical Plant

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Injection Quill



- Injection quill is clogged
- Deposit is wax like and white to brown in color.
- Product injected is chlorine into a clean water line.
- Why a deposit?
- Impurities in the chlorine

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Boiler Boil Out Procedure

> **Scope:** To remove oils, mill scale & piping debris from a new boiler or new boiler tubes – to prevent foaming & carryover.

> **Procedure:**

1. Fill the boiler up to the top of the tubes with warm feed water.
2. Add 2 lbs Sodium Hexametaphosphate for every 1000 gallons of flooded boiler volume.
3. Add 2 gallons of 50% sodium hydroxide for every 1000 gallons of flooded boiler volume.
4. Remove safeties and blank off, fill boiler to the top, close up boiler, and fire off boiler on low load.
5. Heat boiler to 180°F-200°F which starts circulation; maintain this temperature for 3-5 hours.
6. Allow boiler to cool to 120°F then add water slowly to the bottom of the boiler and allow the boiler to drain out of the top (connect hose to the vent line) – this removes floating oils.
7. Once the flush water is clear, drain the boiler.

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ADVANCED DISPERSANT CHEMISTRY Dispersant Interconnected Functionality OPTIONAL COURSE



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Functionality Rules of Thumb

- Three Primary Functional Groups
 - **Carboxylates** (acrylates, maleates)
 - **Sulfonates** (AMPS, Sulfonated Styrene, Other Specialty)
 - **Non-ionics** (acrylamide and derivatives, hydrophobes...)

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Functionality Rules of Thumb

- **Carboxylates**
 - Provide General Purpose Functionality
 - Typical Backbone
 - Good for Dispersion, CaCO₃, CaSO₄

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Functionality Rules of Thumb

- **Sulfonates**
 - Typically for Stabilization of Phosphate, Iron, and Zinc
 - Add Electrolyte Stability



Functionality Rules of Thumb

- **Non-ionics**
 - Extend Functionality to Include a Broader Range of Solids
 - Can Change Polymer Configuration Properties
 - Can be Effective for Stabilization Similar to Sulfonates

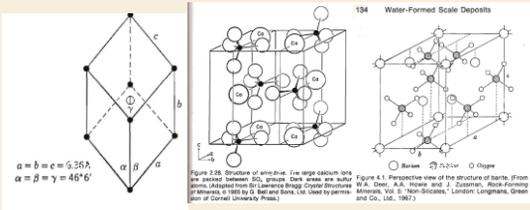


Definition - Crystal Habit Modification

- Crystal Habit is generally defined as the normal size and shape of a precipitated substance in a given set of environmental conditions.
- Crystal growth is dynamic. Crystalloids that do not grow tend to redissolve.
- Polymers and other materials such as phosphonates can modify the size and shape of mineral crystal habits.
 - $\text{CaCO}_3 > \text{Ca}_3(\text{PO}_4)_2 > \text{BaSO}_4 \gg \text{CaSO}_4$
- Crystal Habit Modification is the basis for scale control using polymers
 - Threshold Inhibition
 - Deposition Tendency
 - Surface Adherence



Common Crystal Habits



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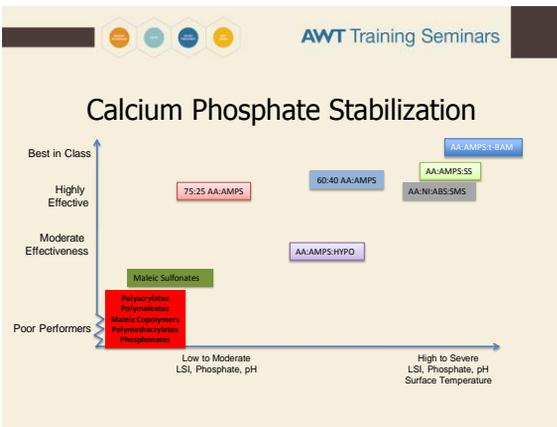
Definition – Particulate Dispersion

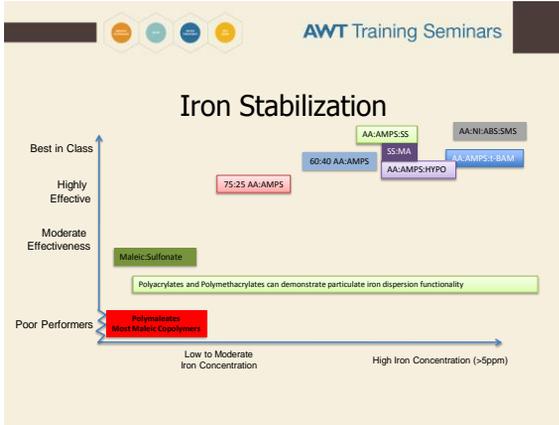
- **Particulate Dispersion (Formal)** - A mixture of finely divided particles, called the internal phase (often of colloidal size) distributed in a continuous medium, called the external phase.
 - Colloidal is where finely divided particles, which are approximately 10 to 10,000 angstroms in size, are dispersed in a manner that prevents them from being filtered easily or settled rapidly.
- **Particulate Dispersion (Practical)** – Suspension of particulates in an aqueous solution.
 - Inorganic
 - Organic
 - Mixture
- **Polymer type and Mw are key determinants in deriving functionality**

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Dispersing Polymer Selection

- **Multiple Functionalities Must Be Considered**
 - Threshold Inhibition
 - Stabilization
 - Crystal Modification
 - Dispersion
 - Chelation
- **Polymers are Engineered for Specific Purposes**
 - No Magic Bullet for All Scale Types





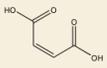


Monomer Properties - Carboxylates

- Carboxylic Acids
 - Typical Polymer "Backbone"
 - Usually the Majority Component
 - Provide Base Functionality
 - Threshold Inhibition
 - Earth Metal Chelation (Calcium, Magnesium, Iron)
 - Solids Suspension
 - Do Not Typically Stabilize Transition Metals
 - Polyacrylic Acids are not Highly Stable to Ca⁺⁺, Ba⁺⁺
 - Maleics are Highly Stable Due to Di-carboxylic Acid and Electrostatic Repulsion

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Typical Carboxylic Acid Monomers



maleic acid

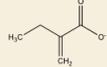


acrylic acid

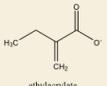


methacrylic acid

Chemical Formula: C₄H₄O₂
Molecular Weight: 99.11
Elemental Analysis: C, 60.59; H, 7.12; O, 32.29



methylmethacrylate



ethylacrylate

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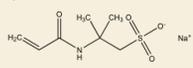
Monomer Properties - Sulfones

- Sulfonic Acids
 - Provide Brine and Hardness Stability
 - Decrease Calcium Carbonate Efficacy
 - Required to Add Functionality for
 - Calcium Phosphate
 - Iron Stabilization
 - Zinc Stabilization
 - Other Transition Metals (Mn, Cu, Ag)
 - Increase Polymer Cost
 - Typically Added at Levels Below 10 mole%

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Typical Sulfonated Monomers

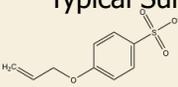
Chemical Formula: C₈H₁₂NNaO₄S
Molecular Weight: 229.23
Elemental Analysis: C, 36.68; H, 5.28; N, 6.11; Na, 10.03; O, 27.92; S, 13.99



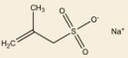
2-acrylamido-2-methylpropane sulfonic acid sodium salt

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Typical Sulfonated Monomers

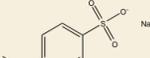


4-(allyloxy)benzenesulfonate
Chemical Formula: $C_{11}H_{14}O_4S$
Molecular Weight: 213.23
Elemental Analysis: C, 30.69; H, 4.25; O, 30.01; S, 15.04

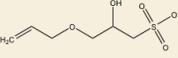


Chemical Formula: $C_5H_9NaO_3S$
Molecular Weight: 158.15
Elemental Analysis: C, 30.38; H, 4.46; Na, 14.54; O, 30.35; S, 20.27

sodium methallyl sulfonate



sodium para styrene sulfonate



3-allyloxy-2-hydroxypropanesulfonate
COPS Monomer

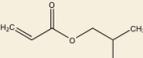
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Monomer Properties - Nonionic

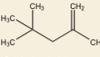
- Non-Ionics
 - May be used as Spacers
 - In-Situ Benefits during Polymerization
 - Can add Quasi Architecture Capabilities
 - Interact with Organics, Hydrophic Materials in Water
 - Biodispersion Properties
 - Increase Polymer Stability to Ions, Hardness

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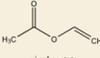
Typical Non-Ionic Monomers



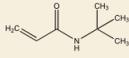
2-hydroxypropyl acrylate



2,4,4-trimethyl-1-pentene
isobutylene



vinyl acetate



tertiary butyl acrylamide



acrylamide

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Simplified Monomer Functionality Chart

	CaCO ₃	CaSO ₄	Ca ₃ (PO ₄) ₂	Iron	Zinc	Organics	Salt Stab
Carboxylate	+	+	-	-	-	-	+ MA - AA
Sulfonate	-	+	+	+	+	-	+ Conc. Dependant
Non-ionic	+ Crystal Mod. - Threshold Chelation	-	+ (HPA)	+ (H ₂ O- Phobic Iron Forms)	-	+	+

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Aqueous versus non-Aqueous

- Impacts Monomer Selection
 - Maleic Homopolymer
 - Non-Ionics
 - Organic Solvent
 - Aqueous
 - Co-Solvent
 - Broader Monomer Selection for Aqueous
 - Sulfonated Monomers
 - Each Process Allows for Specific Process or Initiator Conditions
 - Organic Aromatics
 - Inorganics
 - Cost Weighting
 - Finished Product Purity

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Effect of Molecular Weight

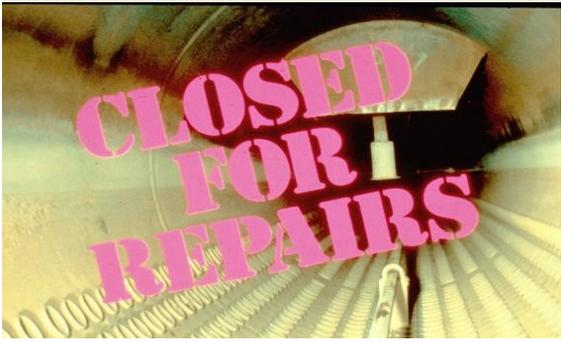
- Polymerization Method Yields Broad Molecular Weight Distribution
- M_w versus M_n
 - Dispersivity
- Rules of Thumb for M_w
 - <5,000 Threshold Inhibition
 - >5,000 Dispersion
 - ~10⁶ Coagulation
 - ~10⁷ Flocculation

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Monomer Combinations

- Holy Grail is Multifunctional Polymer
- It is how we build copolymers
- Usually a Compromise
 - Positive Effects
 - Negative Effects
- Exceptions
 - AA:AMPS® Copolymers

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