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Technical Paper

HIGH PRESSURE BOILER WATER TREATMENT AND ITS CONTROL

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HIGH PRESSURE BOILER WATER TREATMENT AND ITS CONTROL

In the deepsea sector of the marine industry the chemical approach to water treatment and its control for power, propulsion and auxiliary steam generators has been applied for well over 50 years. While steam driven propulsion has given way to diesel engine systems almost exclusively within the general marine market, the large, special application ships such as the LNG, VLCC and ULCC carriers still rely heavily on high pressure steam generators.

In this presentation we will emphasize the special water treatment principles for high pressure steam generator systems in order to accomplish the primary aims of an effective water treatment program. These aims are summarized as follows:

- Maintain maximum equipment efficiency
- Maintain lowest overall operating cost
- Prevent scale and other deposit formations
- Minimize all types of corrosion processes
- Eliminate carryover and contaminant problems

Each of these aims can be applied to any type of steam generating system but they are much more important in high pressure marine systems. In these systems, heat transfer conditions in the express-type boilers are extremely high. Generally, the reference to "high pressure boilers" covers the pressure range at or above 60 kg/cm^2 (850 psig). In these elevated pressure areas, there is a critical need for precise control of water treatment to assure that there are no deposit buildups on high heat transfer boiler areas which can result in catastrophic metal failures and equipment outage.

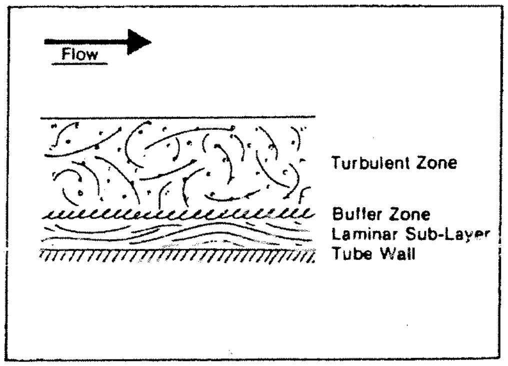
A much more insidious problem can occur in these systems wherein caustic corrosion processes develop on localized heat transfer surfaces in marine boilers where deposits and corrosive action combine to dissolve the steel. This results in severe metal gouging and ultimately expensive failures and lost operational time.

To successfully counteract these processes, the water treatment program for high pressure systems must apply not only to the steam generating units but to the entire water and steam system starting with the preparation of seawater to create a high purity water, through deaeration, chemical dosing and heating before its ultimate use as boiler makeup. The actual internal treating in the high and low pressure steam units as well as the after-boiler system has to be controlled to minimize deposits and corrosion since the condensate is returned to the boilers for reuse.

Because of this system interdependence of the pre-boiler, the internal steam generator and the after-boiler equipment, the chemical treatment applications in all of them will be covered in this presentation. The reason for a system-wide approach to water treatment technology for high performance marine steam propulsion plants is that all areas must function efficiently and be treated properly if the entire program is to be a success.

Focusing on the actual boiler metal surface area where steam generation takes place, there are three distinct types of water flow characteristics in effect in a normal steam generating tube. These are the bulk of the boiler water, the inter-layer boundary and the tube metal surface (see Figure 1). At the interface between the tube wall and the boiler water there is a relatively quiescent layer in which water flow is laminar (streamline). Between this laminar layer and the bulk of the flowing boiler water is a "buffer zone" inter-layer where flow conditions change from laminar to turbulent.

FIGURE 1
Turbulent Flow Boundary Separation at Tube Wall



Of these three flow areas, the most critical is the laminar area adjacent to the metal surface, since it is at this point where aggressive corrosion and insulating deposit formations occur. Either or both of these can drastically affect the boiler system's overall performance. The thickness of the laminar layer is variable and is determined by mass velocity of the circulating water through the tube which is in turn determined by the rate of heat input from the fireside through the metal tube wall.

Chemical conditions and concentrations within the laminar film can be dramatically different from that which are present at any given moment in the turbulent bulk of water flowing in the center of the tube. Flow within the laminar region is usually "streamlined" and heat transfer is by the conduction process. The heat from the metal surface is gradually transferred from the higher temperature area to the lower temperature buffer zone area by molecular diffusion. There is little mixing of the water within the layer and chemical conditions are relatively stable. These static chemical conditions are extremely important, since they can be either good or bad for the water treatment program.

In the buffer zone layer, there is a change from the streamline flow to a turbulent flow configuration. In this layer heat transfer takes place by conduction as well as convection. Within the buffer zone there is some mixing and instability of chemical concentrations. Chemical conditions can vary rapidly as the system load changes which speed or slow the chemical reaction dynamics; and this, too, can be good or bad for the overall program.

In the main turbulent flow area of the bulk water, there is excellent mixing and conduction; and convection heat transfer takes place along with the diffusion of heat through "eddy currents" which form. It is in this area that the steam which has been generated at the metal surface beneath the laminar layer is quickly removed from the site due to the mass water flow which carries the heated water and steam mixture to the main steam disengaging area in the steam drum. The temperature gradient from the tube wall surface to the main turbulent flow zone varies dramatically.

Chemical conditions in the laminar flow area are such that the dissolved solids concentration in the water film can be substantially higher than that in the bulk of the water. This is an extremely important factor in the success or failure of the water treatment program. The quality of the water and the chemical treatment levels in it are designed and regulated to minimize corrosion and deposits and form the heart of the treatment program. It is at this point in the boiler water circuit where the basic treatment reactions take place in and around the bubbles of steam being produced.

In order for a boiling condition to occur on a tube metal surface, adequate heat must pass from the furnace through the tube metal to the inner surface and through the interface between the metal surface and the water. Generally, this results in highly localized superheating of the water next to the metal so as to drive the reaction of steam generation to completion. Anything that interferes with this heat transfer process results in deposit formations, and highly corrosive chemical solutions can develop at the metal surface.

Consider the fact that the temperature of the water in contact with the metal increases rapidly and the excess amount of heat needed to convert the surrounding liquid into steam (the heat of vaporization) produces a certain amount of superheat in the liquid. The normal process is for microscopic steam bubbles that form increase in size and rise through the laminar layer, through the buffer layer and, ultimately, into the turbulent bulk water flow. However, there are times when the generation of the bubbles is such that there may be an accumulation of them at a particular point on the hot metal. The heat input and boiling process in these localized sites can produce high concentrations of dissolved solids which, in turn, deposit to form insulating formations which act as barriers to heat transfer. This will cause metal overheating and tube failure. The entire boiling process ranges from small discrete bubbles to larger steam blanketed, insulated areas as the bubbles coalesce into a continuous film of steam. This steam film acts as an additional barrier to heat transfer. As this transfer barrier effect increases, the internal temperature of the metal tube wall continues to increase. Soon the structural strength of the metal deteriorates; and when this occurs, the tube fails because of the internal boiler waterside pressure.

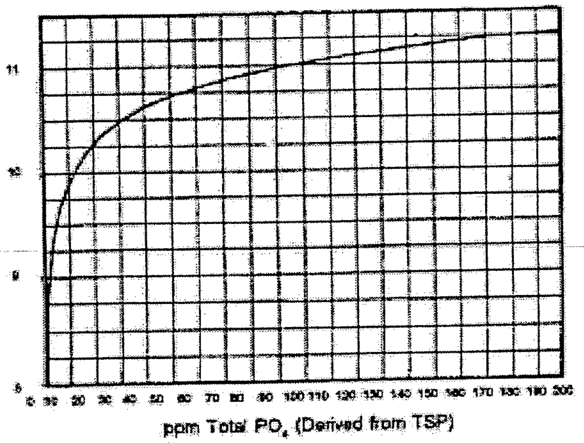
Whether boiler deposits or corrosion occur in highly localized areas or generally throughout a high pressure boiler's main or secondary steam generating sections, the result is the same---metal failure and boiler outage. In high pressure boiler systems the dissolved solids concentrating effect and "steam blanketing" processes can result in deposits under which boiler water can further concentrate increasing chemical levels far beyond normal. Because boiler waters are kept alkaline, the excessive concentrations of the primary alkaline constituent, caustic soda, can lead to "caustic corrosion". In this condition the protective magnetic iron oxide film on the metal surface is destroyed. When taken to extremes this results in relatively large areas of metal loss or "gouging". It does not take long with this occurring before the tube wall is thinned to the point where total failure occurs.

Before "caustic gouging" corrosion can occur, there has to be a concentrating mechanism for the boiler water and, of course, the water must contain caustic (sodium hydroxide). As described above, there is a concentrating mechanism in all heat transfer applications within a boiler, and all conventional water treatment technology programs incorporate caustic alkalinity to produce desirable sludges and minimize acid attack. Thus, both of the prerequisites for caustic gouging are present in boilers. It is only in the higher pressure steam generators (over 60 kg/cm^2-850 psig) that these conditions come together to produce metal failures of a magnitude which demand a different water treatment technology.

In low pressure systems the heat transfer rates and boiler water conditions are such that adequate rinsing of the internal tube surface prevents high localized caustic concentrations along with the high heat transfer rates which result in the chemical gouging and tube failure processes. As such, only the high pressure steam generator systems require the special water treatment programs which utilize the "coordinated phosphate-pH treatment" techniques.

In the shoreside market high pressure boiler system failures and chemical procedures to cure them were examined and developed by several investigators going back to the late 1930's and early 1940's. Once the mechanism of the failures was understood, chemical technology was developed to adjust the water chemistry in the boiler water so that no "free caustic" would exist. This approach resulted in the use of a sodium ortho-phosphate treatment. This chemical hydrolizes in the boiler water producing a combined alkalinity and phosphate which eliminates scale formation and minimizes the "free caustic" which causes the gouging condition (see Figure 2).

FIGURE 2
Phosphate Concentration vs. pH for Trisodium Phosphate Solution



The original development work was done in high pressure shoreside utility plants; and ultimately, the technology was applied in the early 1970's to marine systems with high pressure boiler equipment. Drew pioneered the introduction of this concept within the marine market.

The original shoreside work on the new water treatment process for high pressure boiler water systems involved the use of two sodium ortho-phosphate compounds, either monosodium or disodium phosphate and trisodium phosphate. The system was called "coordinated phosphate-pH control". As the trisodium phosphate hydrolyzes in the water it produces a hydroxyl ion (OH) which controls the pH level of the boiler water (see Figure 3). The monosodium or disodium phosphates do not produce this condition. Therefore, the ratio of trisodium phosphate to one of the other phosphates can be adjusted so that the desired pH and phosphate levels can be attained without creating "free caustic".

FIGURE 3
Phosphate Hydrolization Reactions

1. Trisodium orthophosphate ⟶ hydroxyl ion

$$Na_3PO_4 + H_2O \rightleftharpoons 3Na^+ + OH^- + HPO_4$$

2. Disodium orthophosphate ——— no hydroxyl ion

$$Na_2HPO_4 \rightleftharpoons 2Na^+ + HPO_4$$

3. Monosodium orthosphosphate —— no hydroxyl ion

$$NaH_2PO_4 \rightleftharpoons Na^+ + H^+ + HPO_4$$

Generally, the new treatment program was found to work extremely well in most cases. However, there were still instances where conditions got out of control and failures occurred. The possible causes of these continuing failures were the subject of further investigations throughout the 1940's and 1950's until an apparent cause came to light. It was found that there was a loss of phosphate and an unusual precipitation and deposit formulation of what was previously considered a "soluble phosphate". This occurred in the highly concentrated water boiler within the laminar layer adjacent to the high temperature metal surface in certain boiler tubes. This changed the delicate balance of phosphate and hydroxyl ions within the boiler water which lead to a periodic excess of "hydroxide-ion" in the concentrated liquid which then attacked the surrounding tube metal.

The "phosphate loss" from the boiler water is not readily detectable under normal steaming or operating conditions. However, it is apparent when boiler loads are varied or the equipment is taken out of operation. At these times the "observed" phosphate reserve in the boiler water seems to increase dramatically from that which would be considered normal and in line with chemical amounts dosed. The extremely high, instantaneous phosphate levels during variable load conditions has been called "phosphate hide-out".

The temporary "hide-out" of phosphate is due to the fact that the phosphates which are normally water soluble chemicals can precipitate under certain boiler water conditions. When this occurs there is an upset of the delicate balance between phosphate and pH in the boiler water. This creates deposit formations which obstruct normal heat transfer causing localized overheating and ultimate tube failure.

The original phosphate-pH control worked very well as long as the boiler water treatment program was adjusted properly with frequent monitoring tests. However, since all boiler systems are "dynamic" there still were numerous instances where proper boiler treatment control could not be maintained at the desired phosphate and pH levels required. Deviations from optimum produced highly undesirable conditions and in some cases failures.

One of the reasons for the deviations from recommended levels was found to be the use of two different phosphate materials which prevented complete program control at all times. It was at this point that Drew pioneered the introduction of a "modified phosphate-pH treatment" program called the "ULTRAMARINE℠ System of High Pressure Boiler Water Treatment" in the marine market.

The ULTRAMARINE program revolves around the independent utilization of "disodium phosphate" and "caustic soda" in such a way that no "free caustic" is generated in the boiler water. At the same time, proper pH levels are produced and excessive phosphate concentrations are minimized. This further reduces the potential for phosphate hide-out in the boiler water.

The ULTRAMARINE Program went into effect in the marine industry in the early 1970's. It was quickly recognized as the corner stone of a successful high pressure boiler operation on board ships. It provided a completely flexible water treatment program that matched the extremes in load variation experienced within marine steam generator systems. It continues today as the most effective, proven high pressure boiler water treatment program for all steam generator systems. The details of the ULTRAMARINE-phosphate-pH technology are summarized in Figure 4.

FIGURE 4
ULTRAMARINE Program-Phosphate-pH Reaction

Disodium orthophosphate + Caustic soda ⟶

$$Na_2HPO_4 + YNaOH \longrightarrow$$

(produces an equilibrium with)

⟵ Sodium hydrogen orthophosphate + water

$$\longleftarrow Na_xH_yPO_4 + YHOH$$

where $x = 2.75 + 0.10$
$y = 3 - x$
$Y = 1 - y$

"Free Caustic" is not present in the boiler water with this equilibrium reaction maintained (see Figure 6 for test limits for full ULTRAMARINE boiler water control.

While all of the coordinated phosphate-alkali treatments are specific to the control of "caustic gouging" corrosion and scale deposition in the high heat transfer areas of boilers such as in the water walls, the screen tubes and the main generating tube banks, it must be recognized that there can be water-related problems in other sections of the overall boiler system which can create equipment failures of one type or another. In fact, the proper preparation and treatment of the entire water and steam system from the point at which water enters the vessel as seawater, through the pre-boiler circuits to the actual steam generating processes in the boilers and into the after-boiler steam system must be given full attention. It is not possible to strive to maintain protective conditions inside the boilers while neglecting the pre-boiler water preparation or the after-boiler steam/condensate circuits. There is complete interdependency from one end of the ship's water systems to the other. At this point, it is appropriate to turn our attention to the entire ship's water system related to the high pressure steam generators to get a full appreciation of the importance of a complete water treatment program.

THE PRE-BOILER SYSTEM

The water cycle on a vessel starts with the sea water drawn into the sea chest. From a chemical standpoint, the primary cations (positive ions) and anions (negative ions) in seawater of greatest concern in marine water treatment are shown in Figure 5. These major and minor constituents in the water produce a total dissolved solids concentration of approximately 34,500 ppm (3.45%).

FIGURE 5
Major Seawater Dissolved Solids

• Cations	Symbol	ppm
Sodium	Na^+	10,500
Magnesium	Mg^{++}	1,250
Calcium	Ca^{++}	400
Potassium	K^+	350
Strontium	Sr^+	14
• Anions		
Chloride	Cl	19,000
Sulphate	SO_4	2,700
Bicarbonate	HCO_3	140
Bromide	Br	70
Silica	SiO_2	10

Plus 45 minor substances
Total Dissolved Solids - 34,500 ppm (3.45%)

By far the major constituent in sea water is sodium chloride (common salt). While this constituent can be troublesome in operating equipment, the combinations of hardness (scale-producing) magnesium and calcium compounds can be much more serious. These cations combine with anions such as sulfate and carbonate to form hard scale deposits which are excellent heat transfer barriers. Materials such as silica can be extremely troublesome particularly in high pressure steam generating equipment, since it will volatize from the boiler water and deposit in the propulsion turbines. Fortunately, its concentration is quite low in sea water, and it can be easily controlled.

The first water treatment consideration is to convert the highly concentrated seawater into a very low level dissolved solids water (distillate) suitable for use in high pressure boiler equipment. At the same time, the process of creating acceptable water for boiler makeup produces high quality water for other shipboard uses such as cooling applications and potable supplies.

The most effective method for producing large volumes of high quality water from seawater is a marine evaporator system. Other methods of seawater purification have been examined over the years, but each has some serious drawbacks of one type or another for shipboard use and, as such, we will concentrate this portion of the discussions on evaporation processes.

There are two problems to be overcome in a marine evaporator. The first involves heavy scale formation which reduces distillate output and requires greater heat input in an attempt to maintain the designed water production capacity of the unit. This procedure cannot continue for long, and ultimately the need for chemical and/or mechanical cleaning of the heat transfer surfaces is apparent. The second problem is "brine carryover" which contaminates the distillate produced making it unfit for boiler makeup and other shipboard uses.

Carryover from an evaporator occurs because highly concentrated brine promotes foaming and liquid entrainment in the generated vapor. To counteract the brine contamination of the distillate all evaporators are fitted with passive mechanical "mist eliminators". These eliminators remove the brine from the pure water vapor. Another source of carryover can be the lack of proper water level control which allows excessively high brine levels in the evaporator shell. Such a condition, if allowed to persist, will permit high concentrations of salt water to be carried over with the vapor leaving the unit.

There are many types of evaporator units in service on ships but all function on essentially the same basic principles. Heated seawater vaporizes under sub-atmospheric (vacuum) conditions generating a pure water vapor. The water vapor passes through the mist eliminator which removes the entrained moisture and the purified vapor travels through a condenser which converts the vapor into water. The process is relatively simple but the scale forming potential of seawater is so great that an untreated or improperly attended evaporator system can create large amounts of hard, crystalline scale on its heat transfer surfaces rendering them useless in a very short time. The scale formation reduces heat input and distillate output; and thus, more heat than normal is required to keep the evaporation process going. This is an unacceptable condition and demands frequent periodic cleaning, either chemically or mechanically, to return the heat transfer surfaces to a clean, efficient state. In some units the damage caused by the scaling and cleaning requirements can progress to the point where major parts of the evaporator must be renewed.

Originally, procedures for cleaning evaporator heat transfer surfaces involved either mechanical scraping or "thermal shocking" the hot coils with seawater which cracked the brittle scale allowing some of it to drop to the bottom of the shell. Neither of these processes were satisfactory and the next step was to try chemical treatment of the sea water with phosphates, alkalis and dispersants. This process did work to a certain extent since it eliminated the hard scale characteristics of the deposits. However, it resulted in copious amounts of sludge which in itself adversely affected heat transfer and distillate output.

In the late 1960's Drew pioneered the use of special polymers for evaporator treatment. The chemistry of polymer treatment involves a coating, at the molecular level, on the scale crystals. The scale forming characteristics in the seawater are changed in such a way that the individual crystals neither adhere to themselves nor to the heat transfer surfaces. This process creates a very fluid sludge as the hardness constituents precipitate. This sludge can be easily removed from the evaporator by normal overboard liquid discharge which controls brine density buildup. Another favorable characteristic of the new polymer-type treatment was that it incorporated an antifoam chemical to minimize the foaming tendencies of concentrated brine solution. This dual treatment revolutionized the seawater evaporator operation and practically eliminated the need for cleaning.

The modern evaporator treatment process using polymers is based on the fact that certain dissolved solids in seawater such as calcium sulfate have a "reverse solubility". This reversal means that the dissolved solid increases its solubility characteristics as the liquid temperature rises. This continues up to a certain level (approximately 38°C) after which additional temperature increase dramatically reverses the dissolved material's solubility which causes precipitation of the chemical from solution as a hard scale. This scale forms primarily on heat transfer surfaces. With the polymer treatment it has the effect of destroying the crystal growth pattern of the scale forming constituent and promotes distorted crystals which do not agglomerate or adhere to the heating surfaces. This process effectively eliminates scale deposit formations in the evaporators and maintains their designed water production capacity almost indefinitely.

Dosing the polymer treatment is based on the type of evaporator and the point at which the greatest heat input occurs. If the unit is of the "flash-type", the primary heating of the seawater is done external to the evaporator itself. In this case the polymer treatment is applied upstream of the external heater which keeps its transfer surfaces clean. Since this point of addition is prior to the low pressure area and ahead of an external heater, a proportioning chemical dosing pump will be required to inject the treatment solution.

If the evaporator is of the type where heat is applied within the evaporator shell, the treatment can be dosed directly into that area. As long as the pressure within the shell is below atmospheric, a simple, continuous dosing arrangement employing a gravity feed tank with a flowmeter control is quite adequate.

Continuing in the pre-boiler water system downstream of the evaporator condenser and distillate storage, we essentially have "pure water" from the standpoint of dissolved solids. However, it does contain dissolved gases which can be troublesome if they are not removed. The equipment to accomplish this on high pressure steamships through which the distilled makeup flows along with the returning condensate from the steam and condensate system is the "deaerator".

This unit is fitted with special spring-loaded spray nozzles to atomize the combined distillate and condensate into a steam space raising its temperature which liberates practically all of the dissolved gases from the liquid. These gases are then expelled from the system. The deaerated water droplets fall into a storage section where the water is held for subsequent use as boiler feedwater.

The process of efficient deaeration in a modern deaerator is based on atomization of the water to increase its surface area by many magnitudes within a pressurized high temperature steam space. The "non-condensible" gases are expelled from the water into the surrounding steam. Good atomization and steam temperature control are required for an efficient deaeration operation. Under these conditions the concentrations of the dissolved gases, particularly oxygen, are reduced to extremely low concentrations. The residual oxygen content of the water from a properly controlled deaerator is in the order of 5-7 ppb (parts per billion).

The expelled gases including the oxygen are removed from the deaerator through a vent which takes them out of the boiler system. In some instances, deaerators are fitted with vent condensers which trap steam and gases and convert them into a liquid which is highly corrosive. It is for this reason that vent condenser drips should not be returned to the system. Of course, this does create some heat loss from the system. Trying to recapture some of this loss by bringing the highly corrosive drips back into the system is false economy.

The deaerator's storage section is an ideal point in which to continuously inject treatment chemicals, such as an oxygen scavenger or a neutralizing amine. The most efficient oxygen scavenger for high and low pressure systems has been found to be catalyzed hydrazine which combines with oxygen on a 1 to 1 ratio. Its reaction produces only nitrogen and pure water which are most desirable end products because they add no dissolved solids or objectionable gases to the system. A neutralizing treatment such as morpholene or cyclohexylamine is usually added along with the hydrazine treatment. These secondary treatments are effective since they are volatile amines which pass from the boiler water with the steam and travel to all parts of the system. At points of condensation they combine with any acidic constituents in the condensate and neutralize them.

The equipment between the deaerator and the high pressure boiler is usually in the form of feedwater heaters which increase the temperature of the water to the desired level for its injection into the boiler. Primary boiler water treatments usually are added by means of a chemical proportioning pump to the feedwater line or directly to the boiler's steam drum.

In the boiler the feedwater mixes with the boiler water in the steam drum and descends through downcomer tubes and into the mud drum. From there it flows into the main steam generating sections and into the headers which feed the water wall tubes. As the water passes from the steam drum to the various lower sections of the boiler, it is continuously mixing with the regular boiler water which has already passed through the generating section before. The mixing process distributes the treatment chemicals throughout the water ensuring that the water that is entering the generating sections is up to proper treatment levels. The non-volatile treatments are partially consumed by any contaminants that may be in the feedwater, and a predetermined amount remains in solution as a reserve. The proper level of treatment reserve is based on boiler pressure, experience and a thorough knowledge of the ship's systems and operating conditions.

Volatile materials such as the neutralizing amines evolve from the treated boiler water with the steam which proceeds through the internal steam drum purification equipment. From there it travels into the superheaters and other parts of the steam/condensate system. Some of the oxygen scavenger reserve in the feedwater after reaction with the residual oxygen in the water from the deaerator can break down and produce ammonia gas which passes off with the steam from the steam drum. To a certain extent, even the hydrazine scavenger itself can evolve from the water and travel into the after-boiler sections.

The treated boiler water will come to an equilibrium under normal steaming conditions. When properly dosed and solids controlled by continuous blowdown and a periodic bottom blowoff schedule, the system will satisfy the "Aims of the Water Treatment Program" as previously described. In the ULTRAMARINE^{SM} Water Treatment Program which modifies "the dual phosphate" approach for control of the "Coordinated Phosphate-pH Program", caustic soda is used with disodium phosphate as its main treatment constituent. These chemicals are adjusted to maintain the desired ratio of pH and phosphate so that "no free caustic" exists in the boiler water. At the same time, the phosphate residual is available to combine with any incoming hardness while the pH level prevents corrosive acid conditions or excessive alkalinity levels which could lead to caustic gouging.

The internal treatment of the high pressure boiler system is usually through the shotwise addition of the caustic soda and the disodium phosphate periodically by a chemical proportioning pump or a pressure pot. Routine daily chemical tests are run to determine the residuals of the two main treatment chemicals in the boiler water which are a guide to the need for additional treatment. Blowdown control is determined by periodic checks of total dissolved solids by conductivity which is the best indication of the concentrations of all ionized dissolved materials. Some additional tests are run on the boiler water to provide a cross-check on treatment variations.

Normally, phenolphthalein (P) and Total Alkalinity (T) determinations are used for this purpose and a silica determination is conducted to make sure that its maximum level is not exceeded. Silica is of concern because it is a contaminant in a high pressure system which can volatilize with the steam especially at boiler pressures above 40 kg/cm^2 (600 psig). Because of this possibility, concentrations of silica in high pressure boiler water should be held at or below the 3-6 ppm range. A complete high pressure, UltraMarine Treatment control test summary will be found in Figure 6.

FIGURE 6
High Pressure Water Treatment Control

	Boiler Pressure Ranges	
Test	60-84kg/cm^2	84-102kg/cm^2
pH	9.8 - 10.2	9.8 - 10.0
Phosphate	15 - 25 ppm	10 - 20 ppm
Hydrazine	0.03 - 0.10 ppm	0.03 - 0.10 ppm
Chloride	16 ppm (max.)	10 ppm (max.)
Silica	6 ppm (max.)	3 ppm (max.)
Conductivity	120 mmho. (max.)	80 mmho. (max.)
	Condensate Control	
pH	8.6 - 9.0	8.6 - 9.0
Ammonia	0.5 ppm (max.)	0.5 ppm (max.)
	Feedwater Control	
Iron*	10 ppb (max.)	10 ppb (max.)
Copper*	5 ppb (max.)	5 ppb (max.)
Oxygen**	5-7 ppb (max.)	5-7 ppb (max.)

* Periodic tests run at shoreside laboratory.
**Not a routine shipboart test.

A problem which can arise in any boiler system is the carryover of boiler water with the steam. This condition is particularly troublesome in high pressure boiler systems because they are fitted with superheaters and propulsion turbines which can be seriously damaged or rendered inoperable if deposits from the carryover of boiler water accumulate.

To counter these potential problems practically all high pressure boilers are fitted with internal steam purification equipment located in the steam drum. The generated steam is passed through these purifiers (cyclone separators, chevron baffling, intricate directional baffles, etc.) which mechanically remove entrained water droplets from the exiting steam. Maintaining these units in a tight, deposit-free condition assures the highest quality steam leaving the boiler, entering the superheaters and proceeding to the rest of the steam system. Of course, proper boiler water level control is necessary to make sure that the steam drum and the internal purification equipment are not flooded.

AFTER-BOILER SYSTEM

Once the saturated steam leaves the boiler it flows through the superheater sections and to the turbines. A certain percentage of the steam can be diverted through desuperheaters which remove excess heat so that it can be used in low pressure operations. Regardless of the path of the steam, the volatile treatments which were added to the boiler system travel throughout the steam/condensate circuit to minimize corrosion, especially acid attack, at the points of condensation. At these locations the steam condenses into water as condensate, and any gases such as carbon dioxide which may be present are quickly absorbed in the high purity liquid. As carbon dioxide is absorbed in the condensate, carbonic acid is produced. If untreated, the condensate pH quickly drops to the acid range and attack of the ferrous and non-ferrous metal parts of the condensate system occurs. The metals which are dissolved will be returned to the boiler with the condensate and will create problems with deposits of oxides or, in the case of the non-ferrous metals such as copper, will plate-out to form a corrosion cell on the heat transfer surfaces.

The volatile neutralizing amine which was dosed to the pre-boiler system leaves the boiler with the steam and will condense with the condensate when it is formed. Immediately it reacts to neutralize any acidic condition that has been produced. The neutralization process maintains a proper alkalinity in the the condensate thereby protecting all of the metal systems in the return circuit. Control of this treatment process is by means of a simple test of the alkalinity or pH level of the condensate.

The condensate circuits on ships are complex and there are many points for air inleakage. This brings tremendous quantities of corrosive oxygen into the equipment since air contains 20% (200,000 ppm) oxygen. To counteract this condition, Drew in conjunction with major turbine manufacturers developed a system of "crossover dosing" for the excellent oxygen scavenger, hydrazine. In this system, hydrazine treatment is added, under normal running conditions, to the crossover line between the high and low pressure turbines. The treatment dosage is controlled to maintain an adequate reserve of oxygen scavenger in the low pressure steam and condensate circuits. This scavenger addition is a companion treatment to the neutralization amine process.

The crossover dosing system is controlled in such a way that a dilute oxygen scavenger (hydrazine) is injected into the steam throughout normal running conditions. But when boiler load levels decrease, particularly in a maneuvering mode or during in-port time, the control system cuts off the crossover dosing process and redirects the hydrazine oxygen scavenger solution to the storage section of the deaerator.

While the original crossover designs were suited to normal operating and maneuvering load conditions, special circumstances arose in the early 1980's when high pressure ships were run on a "slow steaming" basis. Under these operational conditions the new reduced loads necessitated adjustments in the crossover dosing control program so that the switch of treatment dosing location would not take place during the "slow steaming" process.

While "slow steaming" practices were a necessity at that time due to the economics of world business conditions, they created many problems because of the inability of the high pressure steam systems to cope with the reduced flow rates in the water, steam and condensate circuits. Several problems occurred in the boilers, particularly in the water wall and screen tube areas in which inadequate water flow rates and poor metal surface rinsing produced deposit buildup at points of high heat transfer. Also, there were other major problems within the dynamic pattern of water flow throughout the boiler such as the reduced thermal driving forces between the upcomer and the downcomer tube sections of the main generating bank. In the steam/condensate system there were further problems because of "super-cooling" of condensate. This created additional air inleakage potential and increased corrosion from oxygen. Overall, the "slow steaming" practices were extremely difficult on normal boiler water conditioning techniques. Since flow patterns were disrupted, representative water sampling was affected and proper treatment levels in many areas of the operating units could not be maintained.

CHEMICAL TESTING AND CONTROL

A proper water treatment program necessitates the routine testing of cooled representative water samples from important parts of the boiler steam and water circuit. The collection of water samples from the steam drums of operating boilers will provide for the tests of the volatile and non-volatile constituents. The boiler water treatment control levels are to be held within the limits previously recommended in the ULTRAMARINE Program summary (Figure 6). Samples of cooled condensate should be obtained regularly for pH determinations so that adjustments in neutralizing amine dosing can be made as required.

If a vessel is fitted with a separate low pressure steam generator, the same primary water treatment chemicals can be used as in the high pressure circuit. However, the low pressure steam generator treatment control limits are substantially different from those used in the high pressure system. Generally, in the low pressure system, controls are based on a hydroxide alkalinity. This is determined by Phenolphthalein (P) and Total (T) Alkalinity readings which produce the desired residual alkali level in the water. Also, there are different requirements for reserve levels of phosphate, oxygen scavenger and volatile amine that apply as well.

Because the low pressure steam generators often are fed a mixture of distilled makeup and returns from potentially contaminated steam condensate circuits, there may be a need for supplemental chemical treatments to maintain the equipment in the best operating condition. These supplemental chemicals are not used or needed in the high pressure steam generators. Many of the supplemental compounds for low pressure systems are organic products such as coagulants or dispersants which could be decomposed if they were to be injected into the high pressures boilers where pressures and temperatures are at substantially elevated levels.

BOILER LAYUP

In any marine steam generating system, undesirable conditions can occur which are beyond the scope of normal water treatment practices. Generally, water treatment programs are designed for operating equipment which is in a dynamic mode. However, when either high or low pressure steam generators are put into a static layup of short or long durations, the normal treatment chemicals and the control limits cannot provide adequate protection. This is particularly true in "wet layup" conditions where equipment may be left partially filled with water. While the full subject of protection of boiler systems in layup is beyond the scope of this particular paper, the following highlights will give the reader some of the important considerations:

- Several days before a steam generator is to be taken out of service, the rate of blowdown should be increased about 50 to 100% from that which would be normal. The bottom drum and water wall header blowoff connections should be opened for a series of short blows when boiler load conditions permit. In this way suspended material in these sections will be removed.
- When the boiler is taken off the line, it should not be drained until the pressure drops to atmospheric. This will prevent very hot sections within the boiler from baking on any sludges which may be still in the water circuits.
- If the boiler is to be drained and opened, it should be immediately washed from the top down with a high pressure water hose. This will remove most of the loose materials which may have accumulated during the draining process.
- A boiler should never be laid up or returned to service in a dirty condition. Any accumulated deposits can be extremely damaging as heat transfer barriers and sites for severe underdeposit corrosion when the boiler is returned to operation.
- If the boiler is to be maintained in a wet layup condition without draining and cleaning, we recommend that the water level be increased to completely fill the steam drum and into a special head tank fitted temporarily above the drum vents. During the filling process, additional hydrazine oxygen scavenger should be added to the water to increase the scavenger level to the range of 150 - 200 ppm. The filling of the boiler will eliminate a water level and the increased scavenger concentration will provide layup protection from corrosion due to oxygen.
- When a boiler has been in wet layup with an elevated treatment level the oxygen scavenger, hydrazine, will be vented from the system during the unit's reactivation procedure.

SUMMARY

In summary, we have attempted to present a broad overview of high pressure boiler and feedwater systems and their treatments as they apply to marine steam propulsion plants. As in all water treatment programs, the proper application of treatment chemicals and their control are a necessity if optimum conditions are desired. As routine control tests are conducted, they should be recorded on log sheets for record and review at regular intervals by the ship's water engineering management and the treatment consultant's representatives.

Periodic water samples should be collected from the system for shoreside analyses. This will make sure that conditions on board are being kept within normal parameters. Also, shoreside laboratories can conduct special tests which cannot be run effectively on board. Again, we wish to emphasize that the water treatment program extends throughout the ship's water circuit, and there is an interdependence of one part of the system on all of the others which cannot be ignored.

If the raw seawater is properly treated in the evaporator the distillate dissolved solids are reduced to extremely low levels. If the deaerator is functioning properly and removing the non-condensible gases, the corrosion potential these gases create is reduced to very low levels. If the primary water treatment chemicals for the high pressure boiler are dosed and maintained within the prescribed limits for pH and phosphate reserve, there will be no "free caustic". This eliminates the potential for "caustic gouging" and for objectionable scale deposits. If the volatile treatment chemicals are maintained at recommended levels, the steam and condensate system will be protected from corrosion of the ferrous and non-ferrous metals. This will extend the life of the equipment as well as minimize internal boiler problems caused by the metal oxides being returned with the condensate.

Finally, the proven success of the ULTRAMARINE^{SM} Water Treatment Program and the effectiveness of the chemical control processes especially designed for the marine high pressure steam propulsion plant are notable in that they have been applied in well over 500 ships during the last 20 years. In particular, the modified coordinated phosphate-pH treatment pioneered by Drew Marine has had an excellent "track record" which is still being practiced in almost 150 high pressure ships. It is applicable now and will be in future high pressure boiler systems which may be constructed, since it is flexible and can be adapted to changes in steam generation equipment design or in water treatment techniques. The "Aims of a Water Treatment Program" for today's high pressure ships or those which may be constructed in the future remain the same and can be satisfied by the system-wide techniques presented in this paper.

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