DISTRIBUTED TO R. WESTERMAN 5/6-83.
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RESULTS OF DEVIATIONS FROM FEEDWATER, BOILER WATER, STEAM AND CONDENSATE LIMITS USING LOW HYDRATE ALKALINITY PHOSPHATE AND COORDINATED PHOSPHATE-PH TREATMENTS

Parameter	Description of Condition	Effects	Remedial Actions
A. pH Deviations			
1. pH decreases from limit range with phosphates in limit or increasing.	a. Low hydrate alkalinity phosphate treatment normal pH range for boiler water is 11.0-10.5. pH can decrease out of limit and phosphate remain in limit or increase. This is caused by feeding acid phosphate or by acid contamination within the cycle. pH can shift down to pH 9.7-10.5 range.	a. Shift from low hydrate phosphate treatment range to coordinated pH range 9.7-10.5. This results in no damaging effects to boiler, provided that the pH does not continue to fall. This may cause a change in the nature of hardness deposits.	a. Feed caustic soda to return to pH range limits. Check chemical feeds for acid phosphate and eliminate or reduce feed rate. Check for acid contamination in boiler cycle and eliminate.
	b. As pH continues to decrease into the pH range 9.7-9.0, it is a sign that alkaline phosphate is being converted to more acid phosphate. Causes of increased acidity are the same as above.	b. Lower pH shift is causing a loss of alkaline phosphate buffering capacity against corrosion. Some sludge adherence and deposit may occur below 9.5.	b. Feed trisodium phosphate or caustic soda immediately and blow down. Check for acid phosphate or acid contamination as above.
	c. pH may continue to drop with continued conversion of alkaline phosphate to acid phosphate into range 9.0-7.5. Lower pH ranges dangerous.	c. This level of pH drop will increase general corrosion due to loss of protective magnetite oxide film on boiler steel through solubilization. There is complete loss of protective alkaline buffering capacity at pH 7.5. This is accompanied by rapid corrosion with possible precipitation of acid phosphates and impurities forming deposits. Corrosion and overheating tube failures are probable if condition is not corrected.	c. Feed caustic soda immediately and increase blowdown. Drop load on boiler to 80% or remove it from service. Check for acid-type contamination.

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Parameter	Description of Conditions	Effects	Remedial Actions
A. pH Deviations (Cont'd.) 1. pH decreases from limit range with phosphates in limit or increasing (Cont'd.)	d. pH continues to decrease with acid pH range developing in boiler water-pH range 7.5-4.5 is extremely dangerous to operate.	d. Rapid corrosion of boiler metal ensues with production of hydrogen. Hydrogen embrittlement is possible. Solution of oxide, deposits and metal wastage. Tube failures imminent.	d. Act immediately to feed caustic soda to boiler in large amounts. Blow down and reduce boiler load to bare minimum or remove it from service. Check for source of acid contamination or injection and eliminate.
	e. When pH is 4.5 or below there is free mineral acid in boiler. This is an extremely dangerous range in which to operate.	e. Extremely corrosive boiler water conditions with production of hydrogen and hydrogen embrittlement probable in higher pressure units and possible in lower pressure units. Damage can occur in thirty minutes operating time and tube failures in two hours at the highest pressures.	e. Act immediately to feed caustic soda to boiler. Remove boiler from service. Blow down while adding caustic soda. Check for source of acid contamination and eliminate. Plan chemical cleaning of boiler as soon as possible.
2. pH decreases out of limit and phosphate decreases out of limit	a. With low hydrate alkalinity phosphate boiler water treatment, the normal pH limit range is 10.5-11.0. With a decrease of pH to 10.5-9.7 the coordinated phosphate range is entered. Phosphate would decrease correspondingly from 40-20 ppm to about 25-10 range. Caustic alkalinity is consumed. This could be due to evaporator carryover, main condenser leak or other seawater leaks into the cycle. Excessive blowdown or boiler tube leaks could also contribute to this condition.	a. Salinity meters will indicate leaks or carryover, and chlorides will increase. Conductivity or dissolved solids will increase. Hardness sludges will form. Deleterious effects will not result unless conditions worsen. Lack of chloride increase in boiler water indicates cause is not seawater contamination.	a. Increase boiler blowdown and add phosphate and caustic to limits. Isolate and correct source of seawater ingress to cycle. When there is no chloride increase in boiler water, check for open or leaking blowdown valves or leak in boiler. Add chemicals.

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Parameter	Description of Conditions	Effects	Remedial Actions
A. pH Deviations (Cont'd.) 2. pH decreases out of limit and phosphate decreases out of limit (Cont'd.)	b. A continuation of the foregoing contamination or carryover condition will decrease phosphate to 5 ppm or less with pH range of 9.7-9.0	b. Salinity meters will indicate leaks or carryover and chlorides will increase. Conductivities and dissolved solids will increase. Free hardness may be present in boiler water. Hard scale deposits can form, as well as striking sludge buildups. Loss of protective alkaline buffering capacity. Tube blisters and failures possible with continued boiler operation. If due to blowdown or boiler leak, conductivity will decrease. Conditions will approximate congruent phosphate treatment.	b. Add alkaline phosphates (TSP or DSP) and/or caustic to return to limits. Increase blowdown. Isolate and correct source of leakage or carryover of seawater and correct. If no increase in chlorides and a decrease in conductivity, add chemicals to limits. Check for source of loss of boiler water and correct.
	c. Above-described condition continues. When pH decreases to pH range 9.0-7.5, phosphate alkalinity is depleting rapidly and is about gone at pH 7.5. This is a dangerous condition in which to operate.	c. All of the above factors are intensified, with dissolution of protective magnetite film occurring at lower pH levels of range indicated, and corrosion.	c. Act immediately to correct. Take same action as in b. Lower load or remove boiler from service if possible.
	d. Below pH 7.5 mineral acid is being formed and phosphate alkalinity is depleted. At 4.5 mineral acid is present in the boiler water.	d. All of the above effects are intensified with more rapid corrosion. Hydrogen is produced and hydrogen embrittlement is possible in boiler steels, particularly in highest pressure boilers. Deposits, oxide film, and metal are solubilized. Damage to boiler can occur in 30 minutes or a few hours, depending on conditions.	d. For increased boiler water chlorides condition, act immediately to feed caustic soda and increase blowdown. Remove boiler from service. Check for source of leakage into system. Chemical cleaning may be required. For no change in chlorides, act immediately to feed caustic soda and phosphate. Remove boiler from service. Check for cause of water and chemical loss. Chemical cleaning may be required.

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RESULTS OF DEVIATIONS FROM FEEDWATER, BOILER WATER, STEAM AND CONDENSATE LIMITS USING LOW HYDRATE ALKALINITY PHOSPHATE AND COORDINATED PHOSPHATE-pH TREATMENTS

Parameter	Description of Conditions	Effects	Remedial Actions
A. pH Deviations (Continued) 3. pH increases out of limits and phosphate stays in limits or increases	a. If coordinated phosphate treatment is being used, the treatment will, because of the stated deviation, shift up to a low hydrate phosphate treatment. pH may rise from 9.7-10.4 range to 10.5-11.0.	a. This would cause no deleterious short-term effects unless the boiler surfaces contain heavy deposits for concentrating caustic and resulting higher solids.	a. Add more acid phosphate such as disodium phosphate or hexametaphosphate instead of trisodium phosphate, and reduce caustic if it is being fed. Increase blowdown.
	b. If pH rise continues above 11.0 free hydrate alkalinity is increasing due to caustic soda overfeed.	b. This can result in caustic attack in perhaps several months' operating time, depending on boiler condition and pressure. The higher the pressure of the boiler, the more severe the effects will be.	b. Add more acid phosphate such as disodium phosphate or hexametaphosphate instead of trisodium phosphate, and reduce caustic if it is being fed. Increase blowdown.
		c. In both a and b the effects will be as follows: pH increase. Conductivity and dissolved solids increase. P and M alkalinity increase. 2P-M is a positive number.	

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Parameter	Description of Conditions	Effects	Remedial Actions
B. **Phosphates Deviations**	a. Phosphates are in excess of limit range with pH normal due to phosphate overfeed.	a. Short-term effects normally are insignificant. Long-term effects could be serious due to carryover and undesirable deposits in higher pressure boilers.	a. Stop or reduce phosphate feed and blow down to limit.
	b. Phosphates in excess of limits with pH in excess.	b. Foaming probable, due to high solids and alkalinity with deposits in steam lines and associated equipment.	b. Stop or reduce addition of phosphate and caustic and blow down to limit.
	c. Phosphates above limits and pH below limits.	c. Refer to low pH effects.	c. Add caustic and reduce phosphate to limits by decreasing feed and increasing blowdown.
	d. Phosphate below limits with pH normal.	d. Reduced buffering capacity against pH change and possible undesirable deposits in event of contamination.	d. Increase phosphate feed using less alkaline compound (disodium form).
	e. Phosphate below limits with low pH excursion.	e. Refer to pH deviations.	e. Refer to pH deviations
	f. Phosphate variations with boiler load shifts - "Hide-out". Phosphate decreases with increasing load and reappears with load drop due to concentrating effects.	f. Difficult phosphate reserve control.	f. Maintain clean steam generating surfaces.

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Parameter	Discussion
C. Chloride Limits	The purpose of the chloride maximum limit is to set it low enough that a minor condenser leak or minor evaporator carryover condition would leave sufficient phosphate reserve to protect the boiler. The chloride ion itself has no deleterious or damaging effects if control limits are maintained. Its presence is an indication of seawater inleakage. If maximum limit is exceeded, the blowdown and chemical feeds - caustics and phosphates - should be increased to compensate for hardness intrusion and loss of alkalinity. Leakage source should be located and corrected. If chlorides increase sufficiently to carry over in the steam, they can be particularly damaging to turbine stainless steel components through pitting attack. Catastrophic intrusion of seawater can damage boiler and turbine immediately.
D. Silica	Silica has little effect when present in boiler water below expected ranges and maximum values. When present in excess beyond maximum limits, the silica is solubilized in the steam. This can cause silica deposits on turbine blading. This is a long-term type problem. High silica levels can under some conditions contribute to the formation of hard scales on boiler surfaces in combination with other constituents. This can lead to overheating from very thin highly insulating type silica scales.

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Parameter	Discussion
E. Dissolved Oxygen	Oxygen feedwater levels should be kept strictly within limits. When oxygen is detectable in excess of limits, this can stimulate corrosion of steel in the feedwater cycle and in the boiler economizer during operation. Usually this can be minimized by chemical oxygen scavenger, but not eliminated. The further out of limit the oxygen is, the more likely the chemical scavenger will not accomplish its purpose. Boiler pitting from oxygen without corresponding attack in the economizer can be attributed to downtime with improper layup or treatment of the boiler. Dissolved oxygen creates metal oxides in the condensate and feedwater cycles which carry into the boiler and create deposit accumulations. In the presence of ammonia and excess dissolved oxygen, copper alloys are also attacked. Dissolved oxygen can result from the following: 1). Condenser and turbine air inleakage 2). Deaerator malfunction 3). Pump seals and valve packings 4). Piping leaks under vacuum Effects of dissolved oxygen feedwater levels can be summarized as follows: 1). Less than 7 ppb corrosion is not significant. 2). Between 7 - 15 ppb corrosion is usually mild. 3). Between 15-30 ppb pitting corrosion can be expected in economizer. 4). Above 30 ppb pitting in the boiler may occur.
F. Sulfite	Sulfite is used frequently in lower pressure marine boilers as an oxygen scavenging chemical reacting with oxygen in a ratio of 10 to 1 to form sodium sulfate. It provides a chemical flywheel in the boiler water and protects the metal from oxygen intrusion. In higher pressure boilers, it begins to break down via auto-oxidation to sulfur gases such as sulfur dioxide and hydrogen sulfide. These gases collect in the steam and can cause attack in the rest of the cycle. Simultaneously, sodium sulfide remains in the boiler water, and if low pH conditions occur metal corrosion takes place. Under normal limit concentrations, sulfur dioxide is formed. At excessively high concentrations of sulfite-hydrogen sulfide is formed. Low sulfite indicates intrusion of oxygen, breakdown of sulfite or excessive blowdown. High sulfite levels are indications of excessive chemical feeding.

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Parameter	**Discussion**
G. **Hydrazine**	Hydrazine is a chemical used for oxygen scavenging in higher pressure boilers, similar to sodium sulfite in its functions. It reacts with oxygen on a one-to-one basis forming nitrogen and water. At high temperatures, hydrazine breaks down to form ammonia and hydrogen. The ammonia concentration must be controlled in the condensate to limit ammonia attack on copper alloys. A continuous feed to condensate can reduce corrosion in pre-boiler systems by forming magnetite on steel surfaces. Low hydrazine indicates oxygen intrusion or breakdown of the continuous hydrazine feed, or excessive blowdown. One significant advantage of hydrazine is that by itself it contributes no solids or conductivity to the boiler water. It does raise pH in the cycle and can increase conductivity somewhat, due to ammonia. Excessive decomposition products of hydrazine and sulfite can be corrosive, and overfeeds should be avoided. Underfeeding permits oxygen corrosion to occur. Hydrazine and sulfite should not be used simultaneously because hydrazine can cause sulfite to decompose to sulfides.