

## **CORROSION IN BOILER WATER SYSTEMS**

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### **ABSTRACT**

A review of the types of corrosion that can occur in the water and steam system associated with boiler water applications will be discussed. This will include oxygen, acidic and caustic corrosion, hydrogen embrittlement and stress corrosion cracking. Additionally, the effect of corrosive chemicals, such as chelants, will be discussed in some detail.

Methods of control of corrosion in boilers will be reviewed including the appropriate internal chemical treatment programs, deaerator and steam line maintenance and protection, as well as mechanical solutions to corrosion problems.

The paper will address problems in low pressure (<300 psig), intermediate pressure (300-1000 psig) and higher pressure utility boilers.

## INTRODUCTION

Corrosion on the waterside of boilers and auxiliary equipment associated with boilers is a result of improper treatment or maintenance of the equipment. Corrosion problems can occur in the pretreatment system, feedwater lines, boiler and the steam and condensate system. All can result in high maintenance costs, costly downtime and expensive replacement of equipment. It is the purpose of this paper to discuss the types of corrosion experienced in these systems and the corrective measures necessary to minimize these problems.

In the boiler itself, the operating pressure and the heat transfer rate are critical factors which affect the level of contamination that can be tolerated in the boiler water to avoid deposition and subsequent corrosion.

## BOILER WATER CONDITIONS

At the high temperatures of boiler water the reaction of water and steel is very rapid. The steel utilized for the construction of boiler tubes can rapidly corrode if conditions are aggressive, as it is less resistant to corrosion than many steels. However, under proper treatment and conditions, a protective magnetite ( $\text{Fe}_3\text{O}_4$ ) film forms on the metal surface to protect it from further corrosion. By adjusting the alkalinity in the boiler, an environment can exist where the oxide film naturally forms and is stable.

The effect of pH on the corrosion of steel is illustrated in Figure 1. This shows that the protective oxide film is soluble above a pH of 13 and below a pH of 5. The optimum pH for minimum corrosion is 9.0 to 11.0. Although these data were obtained under boiler water conditions, corrosion can still occur in boilers under these pH conditions by a concentrating mechanism. It is common for boiler water solids to concentrate at a metal surface under low flow conditions or under deposits. This completely changes the environment in contact with the metal and rapid corrosion can occur.

## TYPES OF CORROSION

### OXYGEN CORROSION

Corrosion in aqueous systems is an electrochemical process involving an anodic and cathodic reaction. The anodic reaction is the dissolution of metal into solution as shown below:



In the presence of oxygen, these electrons are consumed by oxygen by the following equation :



Oxygen corrosion is commonly encountered in the boiler pretreatment system prior to deaeration or with ineffective mechanical or chemical deaeration. It is unlikely in an operating boiler but is often found in idle boilers. Oxygen is a common contaminant in steam systems, particularly in industrial plants with long and complex condensate systems or systems with open condensate receivers. Oxygen corrosion in condensate systems is fairly common.

Oxygen corrosion appears primarily as pitting attack. The surface of the metal is covered with tubercles of hydrated iron oxides. If the tubercles are removed, deep hemispherical pits are noted. Each individual tubercle represents one distinct corrosion cell. The maximum metal loss occurs underneath the thickest layer of corrosion product.

Economizers are a common part of the boiler system that experience oxygen corrosion. The water entering the economizer can contain a high dissolved oxygen content. As the water temperature is increased, the solubility of oxygen in water is decreased and oxygen is released from the water. This results in aggressive oxygen corrosion.

Deaerators are another area where oxygen corrosion can occur. A properly functioning deaerator will produce water with less than 15 ppb dissolved oxygen. However, if the operating temperature or pressure of the deaerator is low, if the unit is not properly vented, and if the internal components are not in proper working order, then higher dissolved oxygen concentrations can occur. This will result in severe oxygen pitting attack of the deaerator. Other factors which can affect deaerator performance are plugged spray nozzles, mechanical problems or improper temperature gradient through the unit. If the deaerator operates with widely varying loads or is subjected to thermal shock or steam hammer, this can also cause

corrosive damage or cracking of welds. A Task Group has been formed to investigate another form of corrosive failure in deaerators, stress corrosion cracking, which can be compounded by the presence of oxygen.

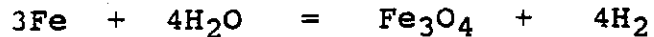
Under normal operating conditions corrosion due to oxygen should not be a problem in the boiler itself. However, when the boiler is drained or when improper storage procedures are utilized, oxygen corrosion can be very severe. The worst condition for corrosion by oxygen is when the boiler is wet and full of air. Under these conditions there is an unlimited supply of oxygen to promote corrosion. When a boiler is stored dry it should be completely dry to prevent corrosion. If the boiler system has non-drainable superheaters or horizontal sections of tube, it may be impossible to drain the boiler and wet storage may be the only solution. When a boiler is stored wet, it should be completely filled with water and an excess of oxygen scavenger maintained in the system.

Oxygen can be present in condensate systems depending on the use of the steam. In a simple power generation system where the condensate system is closed, air is unlikely to contaminate the system, unless the system is down. However, in a manufacturing plant with extensive steam lines and multiple uses for the steam, there are most likely several places for air to contaminate the condensate system. In these cases, oxygen corrosion can be a major problem. It can be diagnosed by the presence of pits and tubercles in the condensate lines, or by the presence of ferric iron rather than ferrous iron in the condensate. If oxygen corrosion is not a problem in the condensate system, but other forms of corrosion are evident, iron in the condensate will be primarily in the soluble ferrous form. Ferrous iron is oxidized to ferric iron in the presence of oxygen. This results in particulate iron oxides in the condensate.

#### CAUSTIC CORROSION

Caustic corrosion is most likely to occur in the boiler itself where a free hydroxide alkalinity is maintained and where conditions exist for the free hydroxide to concentrate in localized areas. The higher the pressure in the boiler, the more likely caustic corrosion is to occur. Caustic attack can be a general thinning or gouging of the metal tube or a cracking of the tube. The latter is often called caustic embrittlement, which is a form of stress corrosion cracking.

Under normal operating conditions the boiler surfaces are coated with a thin protective iron oxide or magnetite film formed by the following reaction:



This film, which is blue-black in color, forms with high temperature under alkaline conditions. If the pH of the boiler water is too low, the formation of the tightly adherent film is affected and corrosion can occur. On the high temperature surfaces of the boiler generating tubes, this protective film protects the metal surface from corrosion. This protective magnetite film can be broken down by chemical or mechanical stress. In strongly alkaline solutions, iron oxides are dissolved to form ferrites. This is a result of iron being amphoteric in nature and causes iron oxide in both acidic or strongly alkaline solutions. To cause caustic attack, the free hydroxide in the boiler has to be concentrated at the metal surface. This concentration of hydroxide can occur locally at the sites of highest heat flux due to steam blanketing or under porous deposits. Concentrations of caustic to greater than 5% are possible.

The thinning caused by caustic attack is often referred to as caustic gouging. White deposits often surround the area of deposition under which the gouging occurs. This problem is most prevalent in boilers of high pressure and high heat flux.

Serious boiler tube failure can occur as a result of caustic embrittlement. This attack is a form of stress corrosion cracking and is sometimes referred to as intercrystalline cracking. Chemical attack of the general metal surface is normally undetectable with a macroscopic examination, but sudden failures can occur when caustic embrittlement occurs. Caustic embrittlement attacks the metal at the grain boundaries of the crystal structure of the metal. It is not necessary to have a high concentration of caustic in the bulk boiler water for cracking to occur, but there is a localized concentration of caustic at the point of attack.

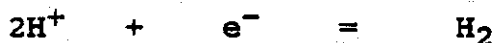
There needs to be two factors present for caustic cracking to occur:

1. High metal stress in the area of attack. This can be present in the boiler tube itself due to the fabrication of the boiler tube.
2. A method of concentration of the caustic to several % at the point of attack. This can occur due to escaping steam in areas where the boiler tubes are rolled into the headers or boiler drum, or in crevices where leakage can occur. Old riveted boilers are particularly susceptible to attack for this reason.

In lower pressure boilers of less than 1000 psig, sodium nitrate has been used as an inhibitor for caustic embrittlement. The ratio of  $\text{NaNO}_3$  to  $\text{NaOH}$  recommended to inhibit corrosion varies from 0.2 to 0.5 depending on the boiler pressure. The lower ratio is used in lower pressures.

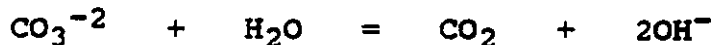
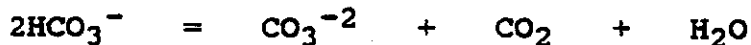
### ACIDIC CORROSION

At low pH, the mechanism of corrosion changes and the rate of corrosion increases severely. The anodic corrosion reaction remains the same, but the cathodic corrosion reaction becomes:

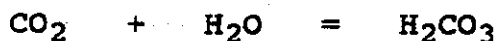


The lower the pH, the higher the concentration of hydrogen ions and the higher the corrosion rate. Under normal operating conditions, the boiler itself operates under alkaline conditions and acid attack should not be a problem. However, if the boiler is acid cleaned, then high corrosion rates will be experienced during the cleaning. It is extremely important after an acid cleaning to thoroughly rinse and neutralize the acid. This will prevent localized high corrosion rates from persisting after the cleaning. Other conditions that can result in acid conditions in a boiler include organic contamination of the condensate which returns to the boiler or ineffective demineralizer operation. If chloride or sulfate leakage is evident in a demineralizer, it is common for the pH of the boiler water to drop at high cycles of operation. This results from the concentration of these ions giving an acidic solution in an unbuffered water.

The condensate system is the one area of the boiler system where acid attack is common. The carbonate and bicarbonate alkalinity in the boiler break down to carbon dioxide as shown by the following equations:



The carbon dioxide then reacts with the condensed steam to produce an acidic solution of carbonic acid:



Carbonic acid attack in condensate systems can be controlled in a number of ways:

1. Treatment with neutralizing amines such as morpholine, cyclohexylamine, diethylaminoethanol etc., which raises the pH of the condensate and eliminates the problem.

2. Use of a filming amine such as octadecylamine which produces a hydrophobic film on the metal surface. This protects the metal surface from the corrosive condensate.

3. Removal or reduction of the alkalinity of the feedwater. This requires the investment of capital for a dealkalizer, demineralizer or reverse osmosis unit.

The carbon dioxide concentration can vary significantly throughout a condensate system. Because of the high distribution ratio of carbon dioxide, it tends to concentrate through the system. As you pass through several pressure reducing units such as flash tanks, the pH of the condensate is lower as illustrated in Figure 2. The initial pH of the condensate in the 600 psig section is 9.5 which is reduced to 8.5 in the 400 psig condensate, 7.5 at 125 psig and 6.5 at 50 psig. Under these conditions, the lower pressure condensate would be highly corrosive. If the condensate receiver is the only area where the condensate pH is monitored, this problem will be missed.

#### **CHELANT ATTACK**

Chelants such as ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are commonly used as the internal treatment of boilers. They are used up to 1200 psig, but more commonly in pressures of 900 psig and lower. They react with divalent metal ions such as calcium, magnesium and iron to form soluble complexes which are removed through the blowdown. Excessive free residual chelants (over 20 ppm) in boiler water can result in severe corrosion of the metal. Chelant attack manifests itself in the form of a shiny uneven surface and a general thinning of the metal.

Under normal operating conditions, a free chelant residual of less than 10 ppm is recommended for safe operation. For the cleanup of dirty boilers somewhat higher levels of 20-30 ppm can be used safely until the boiler is cleaned.

Early use of chelant programs resulted in many problems, but present day technology allows these programs to be used effectively without corrosion.

One item that significantly increases chelant attack is the presence of oxygen, so good deaeration and chemical oxygen scavenging is necessary before the feed of chelants. Severe corrosion in the feedwater lines can result if the oxygen is not scavenged.

#### HYDROGEN CRACKING OR EMBRITTLEMENT

When caustic attack or acid corrosion occurs, hydrogen atoms are formed. The atomic hydrogen can diffuse into the metal surface until it reacts with another hydrogen atom using the metal as a catalyst to form hydrogen gas. This causes cracking in the metal as the hydrogen gas forms. It results in microfissures on the metal surface along the grain boundaries or in more severe cases exfoliation of the metal. This type of attack can be possible after acid cleaning, if there is acid hideout in the system.

#### CORROSION IN IDLE BOILERS

One of the most common and severe types of corrosion in a boiler occurs during storage. When a boiler is taken out of service, even for short periods of time, severe corrosion can occur unless precautions are taken.

There are two methods of storage of boilers, wet and dry. If dry storage is used it is important to remove all water from the system. Special attention needs to be placed on horizontal or non-drainable boiler or superheater tubes. Compressed air is often used for this purpose. Heaters may be necessary to maintain the air temperature above the dew point. In addition, desiccants such as silica gel, activated alumina or quick lime may be necessary to ensure that the boiler remains dry. If there is any water left in the boiler or superheaters, excessive corrosion will occur.

Wet storage is generally preferred for short storage or when the boiler is on standby. In this case the boiler should be flooded and a high residual of oxygen scavenger maintained in the water.

#### CHEMICAL AND MECHANICAL TREATMENT OF BOILERS

The appropriate mechanical and chemical treatment of boiler water is necessary to prevent deposits and corrosion in boilers and trouble-free operation. Operating pressure, heat flux and the method of operation of the boiler play an important role in determining the necessary pretreatment and chemical program.



## PRETREATMENT

The ASME have given a guide to the feedwater limits for feedwater and boiler water as shown in Table I. Above 1000 psig, the requirements for feedwater quality are predictably more strict as shown in Table 2. The type of pretreatment depends on the quality of condensate, amount of condensate returned and the amount of make-up water added to the system. These chemical guidelines give guidance on the quality of water required. Pretreatment can include clarification, filtering, hot and cold lime soda softening, zeolite softening, dealkalization, demineralization, evaporation or deaeration.

As the boiler pressure increases, the more stringent the guidelines and the more emphasis placed on the pretreatment. Demineralization is essential for high pressure boilers and condensate polishing may be necessary to meet the metal limits.

Silica becomes a major factor, particularly with turbine drives.

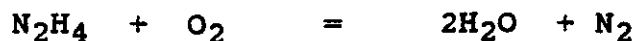
## REMOVAL OF DISSOLVED OXYGEN

We have seen earlier the importance of removing dissolved oxygen from the feedwater. Deaeration is essential for effective operation of a boiler. A feedwater deaerating heater or condenser should be designed and operated for optimum performance. This involves maintaining the integrity of the deaerator internals, operating at the design temperature and pressure, and proper venting. An effective mechanical deaerator should produce oxygen concentrations at the deaerator outlet of less than 10 ppb or 0.01 ppm.

Sufficient quantities of oxygen scavenger should be added to chemically scavenge the remaining oxygen. Sodium sulfite or catalyzed sulfite are commonly used in lower pressure boilers. It reacts with oxygen by the following reaction:



At higher pressures, sulfite decomposes to produce acid gases (at approximately 500 F and greater) and it also adds dissolved solids to boiler water. Therefore, hydrazine or one of several hydrazine replacements (e.g. hydroquinone, diethylhydroxylamine, carbonylhydrazide and others) are used. The reaction of hydrazine with oxygen is shown below:



The reaction products, water and nitrogen, do not add dissolved solids to the water. In addition, hydrazine and several hydrazine replacements passivate the metal surfaces. Above 400 F, hydrazine decomposes to ammonia by the following reaction:



Excess ammonia can cause corrosion of copper alloys in the condensate system.

#### INTERNAL BOILER WATER TREATMENT

The internal boiler water treatment is designed to prevent scale formation in the boiler caused by feedwater contaminants such as hardness, silica and metals. It also controls the alkalinity or pH to maintain a protective oxide film on the boiler water surfaces and in a pH range which is non-corrosive to the boiler metal.

#### PHOSPHATE/DISPERSANT PROGRAMS

Conventional phosphate programs are typically used in boilers at less than 1000 psig. Orthophosphate is added to the boiler water with sufficient hydroxide alkalinity so that the calcium in the feedwater will precipitate in the boiler as hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . This material is less adherent in the boiler and can be readily dispersed using synthetic dispersants. A typical pH of the boiler water on this program is 10.5 to 11.2. Any silica in the water will remain soluble at this pH, but will tend to polymerize at lower pH and form glassy silica deposits. The magnesium preferentially forms a desirable magnesium hydroxide or brucite, or magnesium silicate or serpentine. These can again be readily dispersed in the boiler.

This program is designed to minimize deposition and can be used when softeners are used.

## COORDINATED PHOSPHATE - pH CONTROL

In this program, the pH and orthophosphate residual are controlled so that no free hydroxide is present in the boiler water. Above a mole ratio of 3.0/1 of sodium to phosphate, free hydroxide is present in the water. It is essential to have demineralized water for this program. Typically a mole ratio of 2.6/1 is utilized which corresponds to a pH of 9 to 10 depending on the  $PO_4$  residual. The chart of pH values at various  $PO_4$  concentrations for the coordinated  $PO_4$  - pH control program is shown in Figure 3. The upper curve 1 shows a 3:1 sodium to phosphate ratio, above which free hydroxide exists. A more typical control is at or below Curve 2 where phosphate residuals of less than 20 ppm are used. Typically, a combination of trisodium phosphate ( $Na_3PO_4$ ) and di-sodium phosphate ( $Na_2HPO_4$ ) is used. The ratio can be adjusted to maintain the appropriate control range.

## CHELANT TREATMENT

Chelant treatments were briefly described earlier. They are typically fed through an injection quill made of stainless steel located in the feedwater line close to the boiler. Oxygen scavenger should be fed ahead of the chelant, preferably in the deaerator storage tank. As discussed earlier, low free chelant residuals should be maintained to avoid excessive corrosion.

Chelant/phosphate combinations have also been used with good success with a claim of lower corrosion potential.

## ALL-POLYMER PROGRAMS

All-polymer programs have some of the advantages of chelants without their disadvantages. Chelants typically produce cleaner boilers than phosphate treated boilers as the hardness is kept in solution. The polymers have similar properties without being corrosive at higher feed rates. Good quality feedwater gives the best results with this program.

## CARRYOVER

Carryover is the entrainment of small droplets of boiler water in the steam. Carryover is controlled with proper mechanical equipment such as steam separation equipment in the steam drum and by limiting impurities that contribute to carryover (alkalinity, total dissolved solids and organic contamination which causes foaming). This involves blowing down the boiler to maintain the limits below those shown in Table I.

Silica can vaporize in the boiler and its volatility increases as the pressure is increased. At a pH of 11.3 in order to maintain a maximum silica level in the steam of less than 0.02 ppm as  $\text{SiO}_2$ , the following maximum silica levels are recommended in the boiler water:

Pressure psig	$\text{SiO}_2$ max. ppm
500	50
1000	10
1500	4
2000	1

The volatility of silica increases as the pH is decreased. The silica guidelines shown in Table I for industrial watertube boilers with superheaters, turbine drives, etc. are recommended as maximums for critical service.

### SUMMARY AND CONCLUSION

Care should be taken in all aspects of the operation of boilers to prevent costly corrosion which can result in unscheduled downtime, high maintenance costs and expensive equipment replacement. Care should be taken to ensure sufficient pretreatment to enable the boiler to operate within careful water chemistry control. Under these conditions, a variety of chemical treatment programs can be effectively applied for satisfying boiler operation. Control is the key to success and inspections can be used to determine if and when chemical cleaning is needed.

Specific attention should be placed in bringing the boilers down, lay-up procedures and start-up, as many corrosion problems originate during this period. Chemical cleaning also needs to be done with care to minimize corrosion during the cleaning.

This review paper addresses the types of corrosion that can occur in boilers and methods of treatment to minimize such problems.

TABLE I

BOILER TYPE	OPERATING PRESSURE PSIG	FEEDWATER			BOILER WATER				STEAM PURITY TARGET <sup>2</sup>
		IRON ppm Fe	COPPER ppm Cu	TOTAL HARDNESS	CONDUCTANCE $\mu$ mhos/cm <sup>1</sup>	SUSPENDED SOLIDS	ALKALINITY "M"	SILICA as SiO <sub>2</sub>	
INDUSTRIAL WATERTUBE WITH SUPERHEATERS, TURBINE DRIVES AND/OR PROCESS RESTRICTION ON STEAM PURITY	0 - 300	0.100	0.050	0.300	3500	4	350	150	↑ Depends on Turbine Limitations ↓
	301 - 450	0.050	0.025	0.300	3000	3	300	90	
	451 - 600	0.030	0.020	0.200	2500	3	250	40	
	601 - 750	0.025	0.020	0.200	2000	3	200	30	
	751 - 900	0.020	0.015	0.100	1500	3	150	20	
	901 - 1000	0.020	0.015	0.050	1000	3	100	8	
INDUSTRIAL WATERTUBE WITHOUT SUPERHEATERS, TURBINE DRIVES AND/OR PROCESS RESTRICTION ON STEAM PURITY	0 - 300	0.10	0.05	0.5	8000	10	1000	150	↑ 1.0 ppm TDS ↓
	301 - 450	0.05	0.025	0.3	6500	5	850	90	
	451 - 600	0.05	0.025	0.3	6500	3	850	90	
	601 - 750	↑	↑	↑	↑	↑	↑	↑	
	751 - 900	NG	NG	NG	NG	NG	NG	NG	
	901 - 1000	↓	↓	↓	↓	↓	↓	↓	
INDUS. FIRE-TUBE	0 - 250	0.10	0.05	1.0	7000	800	700	150	1.0 ppm TDS
INDUSTRIAL COIL TYPE, WATERTUBE STEAM GENERATORS	0 - 300	1.00	0.1	1.0	8000	NG	800	150	TDS, ppm 25
	301 - 450	0.30	0.05	0.7	6000	NG	600	100	12
	451 - 600	0.10	0.03	0.5	5000	NG	500	60	10
	601 - 900	0.05	0.02	ND	4000	NG	200	30	0.25
	901 and Up	0.02	0.02	ND	500	NG	100	10	0.1

TABLE 1

**REFERENCE:** Consensus on operating practices for the control of feed-water and boiler water quality in modern industrial boilers prepared by Feedwater Quality Task Group for Industrial Boiler Subcommittee of the ASME Research Committee on water in thermal power systems.

**NOTES:**

1. Specific conductance ( $\mu\text{mho/cm}$ ) at 25°C without neutralization.
2. Practical limits above or below tabulated values can be established for each case by careful steam purity measurements. Target value represents steam purity which should be achievable if other tabulated water quality values are maintained.

**NG** Not Given in Consensus Report.

**ND** None Detectable

**Table 2**  
**ASME Feedwater & Boiler Water Limits**

Pressure	Feedwater			Boiler Water		
	IRON, ppm	COPPER, ppm	Hardness	SiO <sub>2</sub>	Alkal.	Spec. Cond. (umhos/cm)
1001 - 1500	< 0.01	< 0.010	ND	< 2	NS	< 150
1501 - 2000	< 0.01	< 0.010	ND	< 1	NS	< 100

ND, None Detected  
NS, Not Specified



# EFFECT OF pH ON THE CORROSION OF STEEL

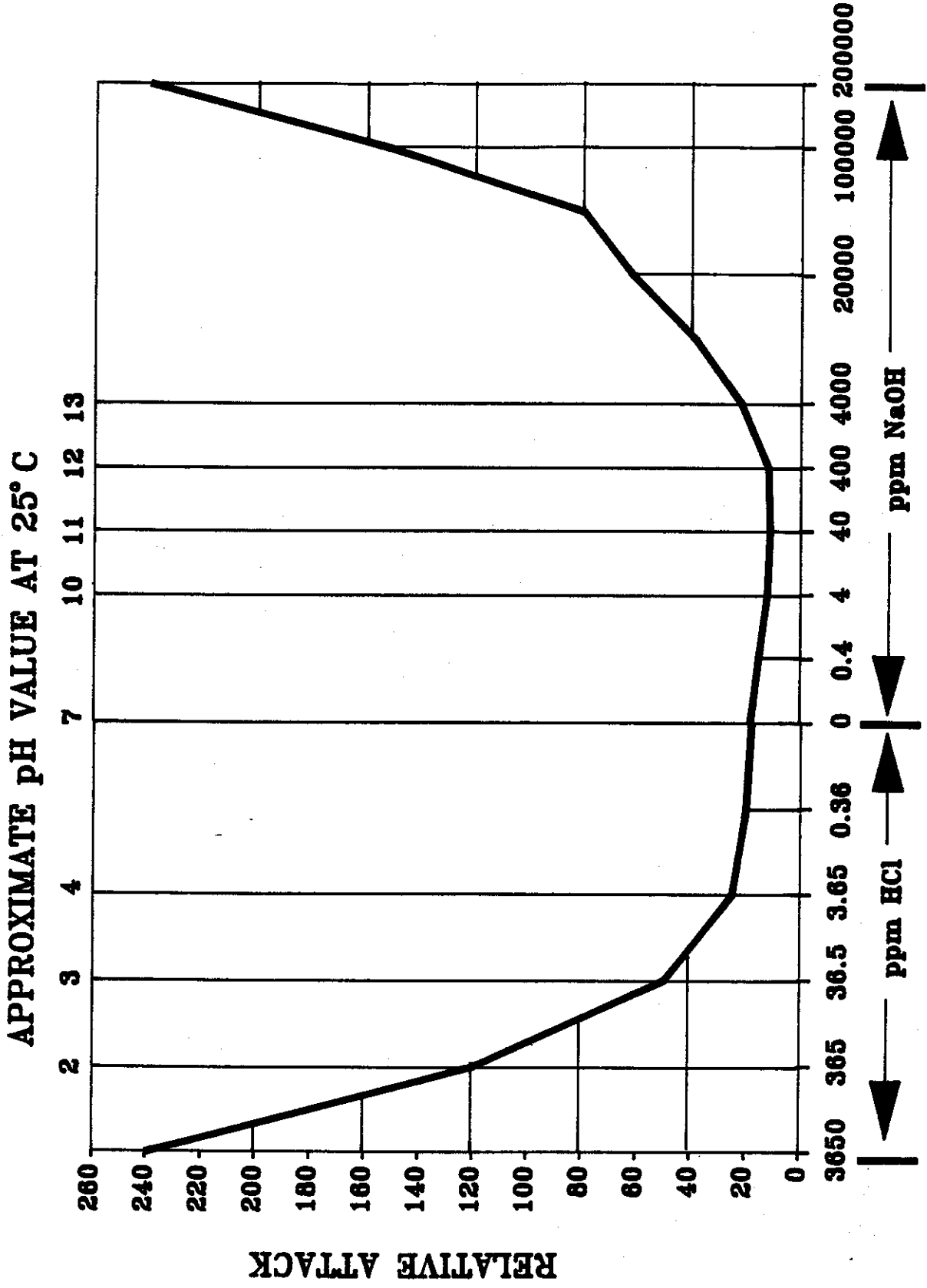


Figure 1

# EFFECT OF PRESSURE REDUCTION ON CONDENSATE pH

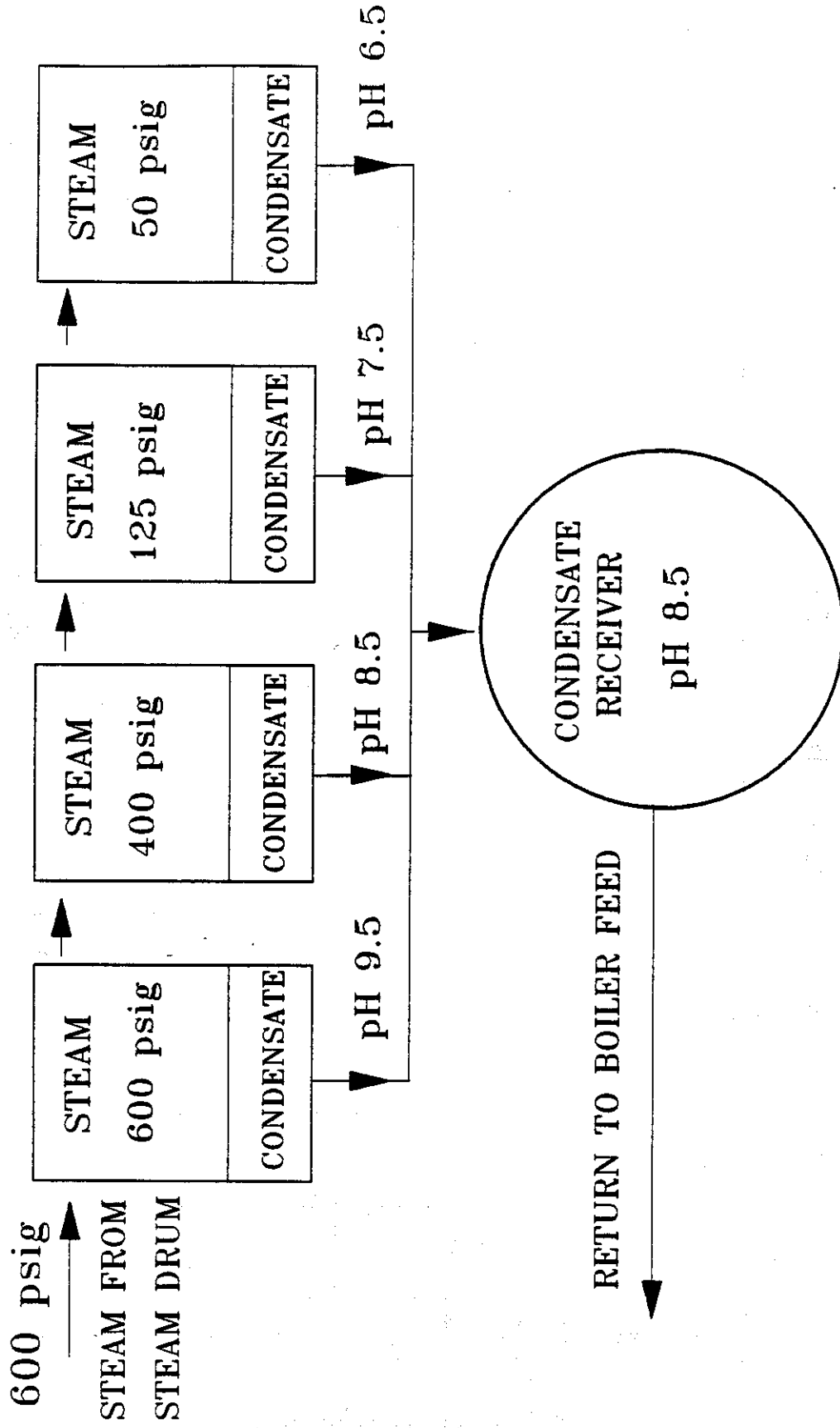


Figure 2

# CURVES FOR COORDINATED PHOSPHATE TREATMENT

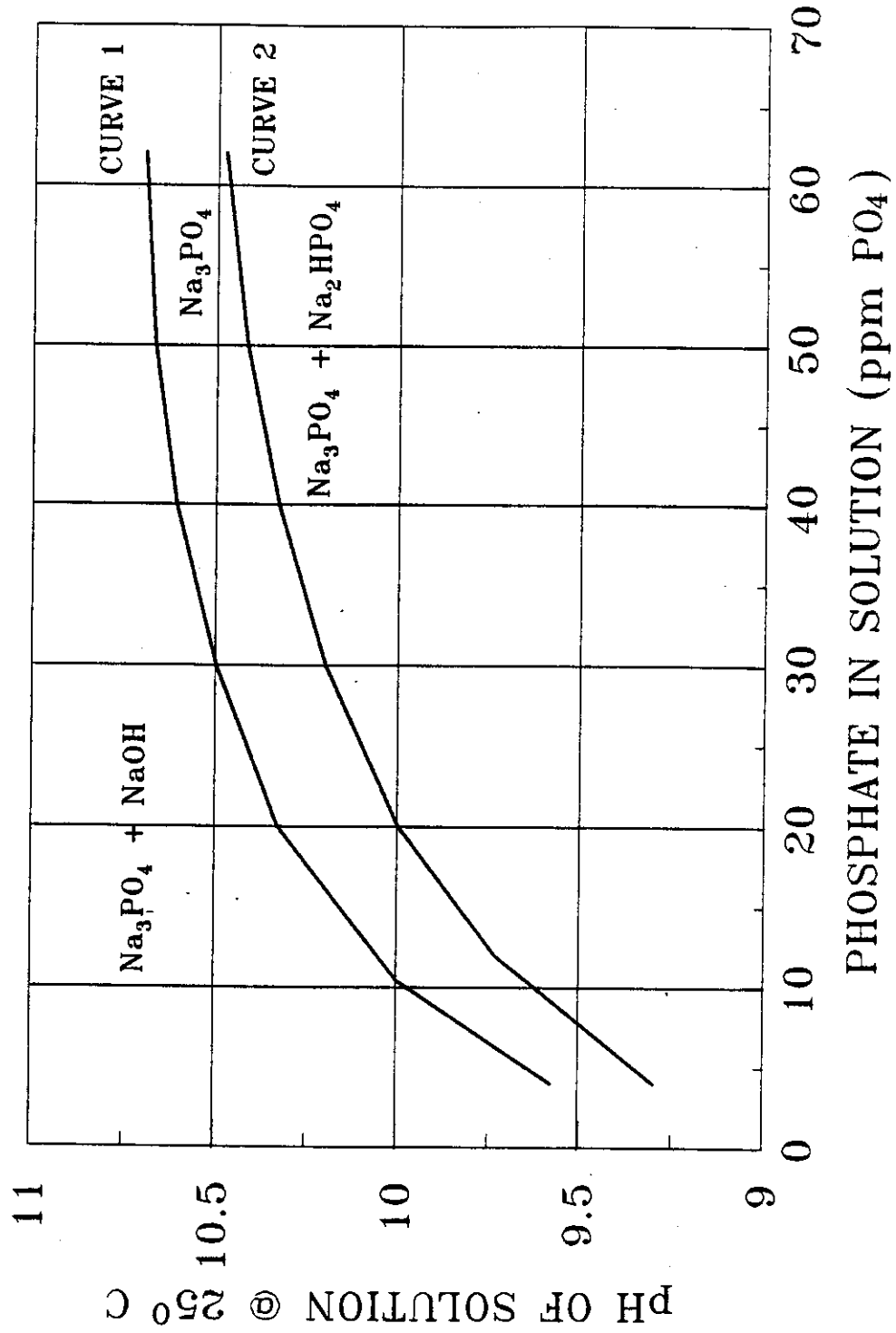


Figure 3