

CORROSION CONTROL IN CONDENSATE SYSTEMS

BY

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ABSTRACT

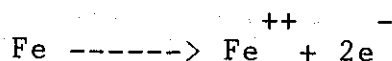
This paper reviews the causes of corrosion in steam condensate systems. The problems associated with condensate corrosion are discussed. Chemical treatment methods for controlling condensate corrosion are outlined. Actual field problems and solutions are presented in case histories.

CAUSES

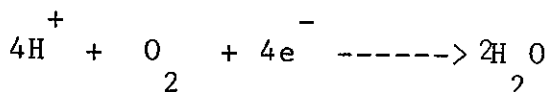
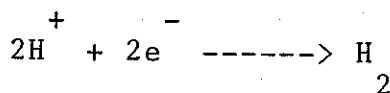
Although there can be a multiplicity of causes of condensate corrosion such as process or cooling water leaks, stressed areas, bimetallic couples and hydrogen sulfide, the primary causes are the presence of carbon dioxide or oxygen gases.

The typical corrosion reactions which take place can be illustrated by the following:

ANODE



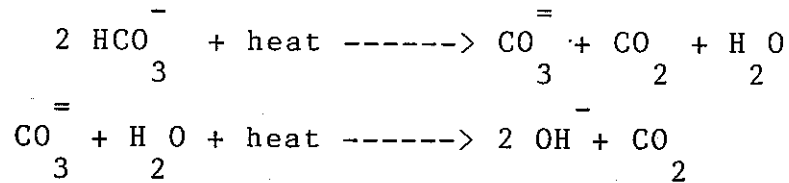
CATHODE



As a part of the normal corrosion process, hydrogen ions in the water are converted to hydrogen atoms by picking up electrons at the cathode. By definition an acid solution (low pH) has a high concentration of the free hydrogen ions available and this will accelerate the cathodic reaction. However, in neutral or alkaline solutions the number of hydrogen ions is reduced and it is possible for a microscopic layer of hydrogen gas to form on the cathode. This hydrogen coating slows down the reaction by preventing the hydrogen ions in the solution from accepting electrons at the cathode.

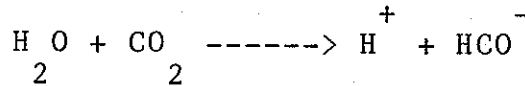
Carbon Dioxide

A major potential source for low pH condensate is from the presence of carbonic acid formed by dissolving carbon dioxide found in the steam. The carbon dioxide results from the thermal decomposition of bicarbonate and carbonate alkalinities in the boiler feedwater. These reactions are:



The first reaction usually achieves 100% completion in the boiler and the second reaction depends on system pressure and boiler load factor. Other sources of carbon dioxide are free carbon dioxide in raw water, soda ash used for internal treatment and decomposition of some organic compounds.

This carbon dioxide is flashed off with the steam and at the point of condensation carbonic acid is formed as shown by this reaction:



The effect of the carbonic acid is to lower the condensate pH causing a general loss of metal resulting in a thinning of the pipe walls. This manifests itself at threaded pipe sections where stress can also accelerate the attack. Carbonic acid also will form ferrous bicarbonate which is highly soluble and has no passivating effect. At pressure reducing stations, the ferrous bicarbonate can revert and ferrous oxide can be precipitated.

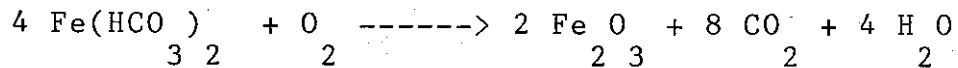
Oxygen

When dissolved oxygen is present in the water, it reacts with the hydrogen at the cathode surface to form water and accelerate the corrosion process. The major source of the dissolved oxygen is from incomplete or inadequate mechanical deaeration of the feedwater or from air inleakage.

The result of oxygen attack is the formation of pits in the condensate systems which proceed rapidly and pipe failures can occur in a very short time.

Carbon Dioxide and Oxygen

When both dissolved oxygen and low pH exist in a condensate system, corrosion rates are accelerated dramatically with the pitting attack taking place in areas already thinned by carbonic acid corrosion. To further complex the problem, oxygen reacts with ferrous bicarbonate as follows:



The release of carbon dioxide by the above makes the corrosion self-perpetuating by forming more carbonic acid.

PROBLEMS

The most obvious problem of condensate corrosion is that failures result; causing needed replacement of piping sections. This adds to the burden of the maintenance load, but more importantly, it can disrupt production with the cost of a shutdown far exceeding any other consideration.

Generally, a plant will "live with" leaks before replacement can be scheduled. A cost not often considered is that associated with steam leakage caused by corrosion. As illustrated by the table below, a great deal of steam can be wasted by steam leaks and that many small leaks in a piping system can easily add up to the equivalent of a single large loss.

TABLE 1

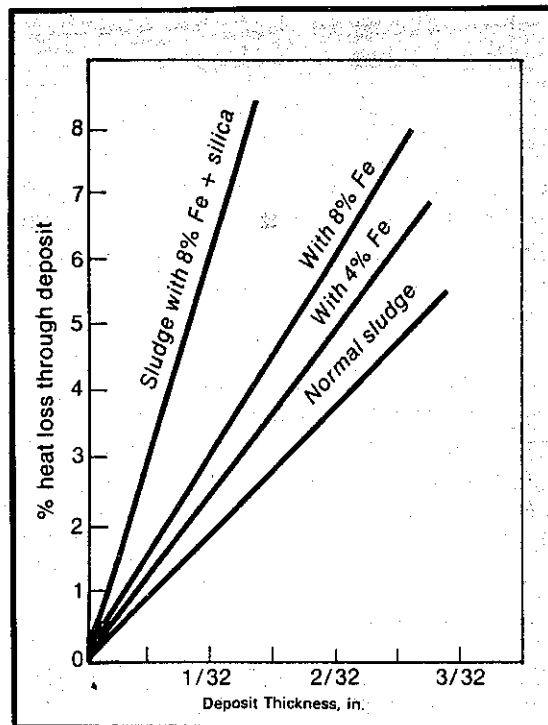
Pressure PSIG	Impact of Steam Leaks in lbs/hr				
	Equivalent leak diameter, in.				
	1/16	1/8	1/4	1/2	1
100	18.2	72.6	290.3	1161.3	4645.1
200	33.9	135.7	542.8	2171.1	-----
400	65.5	261.9	1947.7	-----	-----
850	13.5	545.8	-----	-----	-----

For a 200 PSIG system and a cost of \$2.85/1000 lbs steam, a 1/4 inch leak throughout a year would waste about \$13,554. It would take only 16 - 1/16 inch leaks to be just as costly.

Safety considerations should also be recognized. If leaks occur in high pressure lines, a serious hazard exists which can destroy a plant's safety record by endangering personnel.

The return of the corrosion products to the boiler has a most significant effect and is frequently overlooked. Iron and copper oxides, when present in the boiler water, can act as binding agent for other suspended sludges and promote their adherence to boiler surfaces forming highly insulating deposits. The figure below illustrates the added insulation effect of iron on normal sludge.

FIGURE 1



The most severe consequence of such an insulating deposit is eventual tube failure with unscheduled costly down time and associated lost production. Even if tube failures do not occur, as much as 5% of the plant's fuel consumption can be caused by as little as 1/64 inch of a deposit.

CONTROLLING CONDENSATE CORROSION

A program designed to properly control condensate corrosion must consider removing as much of the corrodents as possible through pretreatment then scavenging the remaining corrodents with the most effective chemical treatment.

Pretreatment - Carbon Dioxide

Since the major source of carbon dioxide in the steam-condensate system can be from the thermal decomposition of bicarbonate and carbonate alkalinities in the feed water, the initial step should be "dealkalization" of the makeup water. Listed below are the mosre common methods available:

- Acidification with Aeration/Deaeration
- Hydrogen Cycle Softening with Aeration/Deaeration
- Split Stream Softening (Hydrogen/Sodium Cycle)
- Hot Process Softening
- Chloride Dealkalization (Chloride Cycle Anion)
- Demineralization

The optimum choice must consider feedwater quality requirements and capital and operating costs. It is possible, depending upon the method, to reduce the potential carbon dioxide to 5 PPM or less. This can minimize the cost to effectively chemically treat the condensate system.

Pretreatment - Oxygen

Although oxygen found in the condensate can be the result of air inleakage, probably the most critical source is oxygen entering with the feedwater. Fortunately, most plants have mechanical deaeration which can reduce the feedwater dissolved oxygen level down to the PPB range. However, being a mechanical device, a deaerator is subject to plugging and mechanical failures and it is recommended that the effluent be checked at least once or twice per year for dissolved oxygen.

A properly functioning deaerator can generally reduce dissolved oxygen to as little as 7 PPB and then chemical scavenging, with one of the following, can be accomplished economically:

- Sodium Sulfite
- Catalyzed Sodium Sulfite
- Hydrazine
- Catalyzed Hydrazine

Chemical Treatment

The current chemical treatment technology utilizes a variety of volatile neutralizing amines or ammonia to counteract carbonic acid corrosion and filming amines and oxygen scavengers to inhibit oxygen attack.

Volatile Amines

Neutralizing amines volatilize with the steam and at the point of condensation the amine dissolves into the condensate reacting with and neutralizing the carbonic acid. Although others have been suggested, the typical neutralizing amines used are:

Morpholine
Cyclohexylamine
Diethylaminoethanol (DEAE)

These amines have two properties which must be considered for choosing the most cost-effective treatment: distribution ratio and reaction stoichiometry.

Distribution Ratio

Distribution ratio is defined as the ratio of the concentration of the amine in the vapor to the concentration in the liquid. The distribution ratio is a function of the pressure and reported values vary as shown below:

TABLE 2

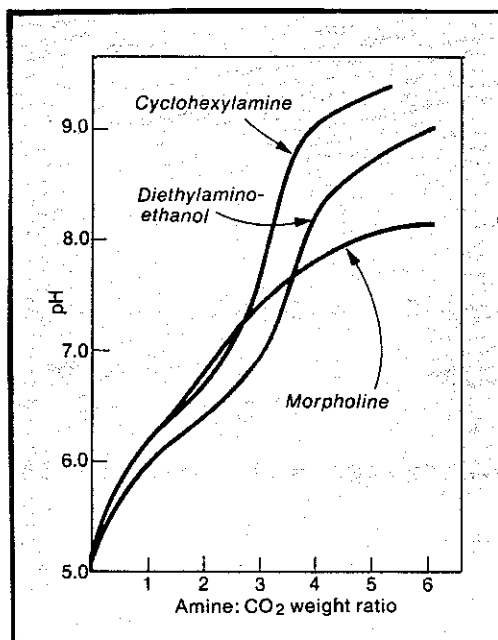
Pressure, PSI	DISTRIBUTION RATIO		
	Cyclohexylamine	DEAE	Morpholine
0	3.0 - 4.0	1.5 - 2.0	0.4 - 0.5
150	9.0 - 14.0	3.2 - 3.8	0.8 - 1.2
300	15.0 - 18.0	4.0 - 4.3	1.1 - 1.2
450	7.0 - 9.4	3.8 - 4.0	1.2 - 1.3
600	6.0 - 6.5	3.6 - 3.9	1.2 - 1.3
900	5.1 - 7.0	3.2 - 3.5	1.2 - 1.3

Note: Variations are a function of the amount of carbon dioxide in the steam.

Reaction Stoichiometry

The neutralizing capabilities, another consideration, is illustrated in the following figure.

FIGURE 2



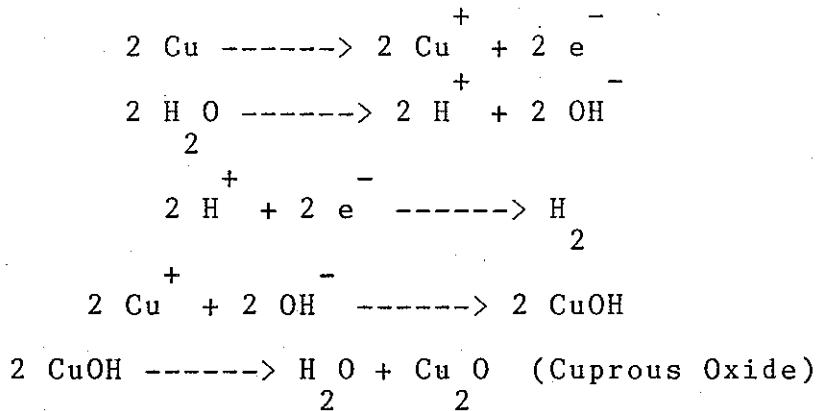
By combining these two properties it is possible to develop blends of amines which will provide needed availability in the early stages of condensation (low distribution ratio) and in distant points (high distribution ratio) while adjusting the pH to the normally desired level of 8.5 to 9.5. Also where feedwater pH adjustment is to be provided with a volatile material, it is seen that a more alkaline neutralizing amine with a low vapor ratio would be desirable.

Generally, Morpholine is used alone in high pressure, low makeup systems as it has little tendency to be lost through vents or from the deaerator. Cyclohexylamine is more suited to lower pressure systems with extensive steam distribution. However, because of the higher distribution ratio, cyclohexylamine easily escapes from vented areas, deaerators and flash tanks. DEAE actually falls between cyclohexylamine and morpholine with respect to distribution ratio but can be costly for pH adjustment. As a result, a blend of amines is frequently used in industrial plants.

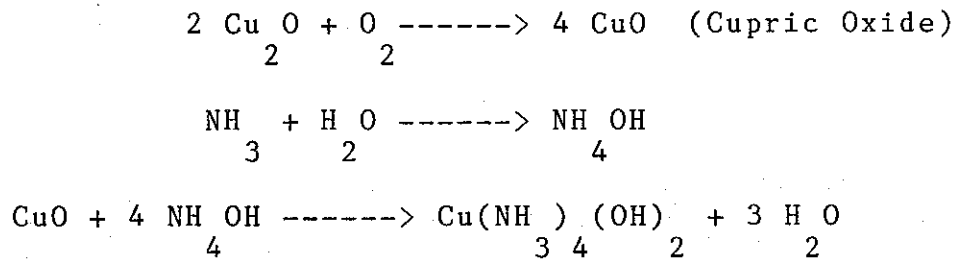
Ammonia

Ammonia which has a distribution ratio of 10:1 at atmospheric pressure which falls continuously to about 3.8:1 at 900 PSI has a neutralizing capability higher than the neutralizing amines. Unfortunately, in the presence of oxygen severe copper attack can result.

The typical reactions for corrosion of copper are:



In the presence of oxygen and ammonia the following reactions can occur:



In the absence of dissolved oxygen cupric oxide is not formed. The concentration of ammonium hydroxide normally encountered in an ammonia treated system will attack cupric but not cuprous oxide.

Either an all ferrous metal system or one in which no oxygen exists could be considered for ammonia treatment to control carbonic acid attack. But care should be exercised any time that copper alloy equipment is involved.

Filming Amines

Filming amines are long chain organic compounds which are actually steam distilled. But instead of reacting chemically they form a monomolecular film on the metal surfaces. Because these amines do not react stoichiometrically with carbon dioxide, they can provide a low cost alternative to neutralizing amines in systems with high alkalinity feedwaters. They also provide a physical barrier that prevents dissolved oxygen in the condensate from coming in contact with the metal surface thus preventing oxygen pitting corrosion.

The affinity of the filming amines to either iron or copper metal or the reduced oxide forms can result in a cleaning activity. If this "cleaning" is too rapid there can be severe fouling of traps and

strainers. For this reason, hydrazine or catalyzed hydrazine is frequently used to scavenge any dissolved oxygen which may be present and also to insure that metal oxides are in the reduced form which insures good film formation.

For optimum results, the pH should be maintained between a minimum of 6.5 and a maximum of 8.6 for octadecylamine and a minimum of 6.0 with a maximum of 8.6 for ethoxylated soya amines.

The normal level of filming amines is based on providing about 1 to 2 PPM based on the steaming rate.

Oxygen Scavengers

Unlike the feedwater, neither sulfite or catalyzed sulfite should be fed to a steam-condensate system as solids would be added. Only a volatile material such as hydrazine should be considered. Using an oxygen scavenger which will also reduce metal oxides in combination with a neutralizing, a filming or a neutralizing + filming amine blend.

will improve corrosion control by:

1. Removing dissolved oxygen minimizing possible attack.
2. Reducing the amount of oxides returned to the boiler.
3. Permitting filming amines to film properly.
4. Reducing cupric oxide to cuprous oxide minimizing possible ammonia attack.

CASE HISTORY NO.1

This southeastern paper mill produces an average of 20 million pounds of steam per day at 880 PSIG and 900°F superheat temperature. The feedwater is 60 percent condensate and 40 percent demineralized makeup water. The metallurgy used in the steam-condensate system includes carbon steel, 70-30 copper nickle, stainless steel and inhibited admiralty.

Previous Treatment and Conditions

Sodium sulfite and a filming amine were used for oxygen scavenging and condensate protection, respectively.

Corrosion of equipment and piping in the after-boiler system had resulted in corrosion products being transported to the boiler causing excessive tube deposits.

The sulfite could not be fed to the storage section of the deaerators because feedwater was used to attemperate high pressure steam and desuperheat low pressure steam. The feed of sodium sulfite was to

the discharge of the feedwater pumps, down stream of the take-off point for attemperation and desuperheating supply. This permitted oxygen corrosion to occur prior to the feed point and possibly past that point due to short contact time. A failure in a closed high pressure feedwater heater supported this theory. Also, the feedwater used for attemperation and desuperheating was suspect of containing unreacted oxygen as the superheaters had excessive magnetite buildup. Testing of condensate for dissolved oxygen revealed oxygen levels that could only be accounted for from air inleakage as it was in excess of that possible from the feedwater alone. Concentrations of iron in the condensate reached 800 PPB and at times copper was as high as 400 PPB. Even with dilution of other condensate streams and makeup water, feedwater levels were still far above the suggested guidelines of 20 PPB of Fe and 15 PPB of Cu.

New Treatment and Conditions

1

2

Catalyzed hydrazine and morpholine replaced the sulfite and filming amine.

During the first phase of the new treatment, both of the new products were fed to feedwater line using the old sulfite feeding equipment. This phase covered about 8 months. Control was maintained to give a boiler water hydrazine residual of 0.05 to 0.15 PPM and a total condensate pH of 8.6 to 9.2. The iron and copper in the feedwater averaged approximately 100 and 50 PPB, respectively.

The second phase which followed a scheduled shutdown, permitted feeding the catalyzed hydrazine and morpholine to the storage section of the deaerators and to the 150 PSIG and 50 PSIG extraction steam. This was acceptable as both materials are volatile and would not cause contamination of the feedwater with any solids. The same controls were maintained as for the first phase. During this period which covered the next 4 months, feedwater iron and copper averaged 200 PPB and 30 PPB, respectively. However, it was found that Paper Machine No.1, during this same period, had an average of almost 460 PPB of iron. This could have represented cleanup of a badly fouled system as by the end of this period this condensate had dropped to about 20 PPB. It should also be noted that by the end of this period the feedwater iron was less than 20 PPB.

The third and final phase followed another scheduled shutdown during which feed points for the paper machines were added. The controls were changed to maintain the feedwater pH between 8.6 and 9.2 with a hydrazine residual of 0.05 to 0.15 PPM by adjusting the chemical feed to the deaerator storage sections. The feed of the mixture of chemicals to the extraction steam was adjusted based on maintaining the evaporator condensate with a pH of 8.6 to 9.2 and having a trace to 0.05 PPM of hydrazine. The feed to the paper machines was

controlled to maintain their condensates with a pH of 8.6 to 9.2 and a hydrazine of a trace to 0.05 PPM. Since that time the levels of iron and copper in the various condensates and feedwater have averaged as shown in the following table.

TABLE 3

SOURCE	IRON PPB	COPPER PPB
Turbine No.1	<10	<5
Turbine No.2	<10	10
Paper Machine No.1	14	<5
Paper Machine No.2	<10	<5
Evaporator No.1	<10	<5
Evaporator No.2	<10	<5
Feedwater	<10	<5

1. Supplied as DREW AMERZINE[®]
2. Supplied as DREWAMINE[®]

CASE HISTORY NO.2

This southeastern phosphate manufacturer has three trains of evaporators in the phosphoric acid plant which receive steam from boilers using a high bicarbonate sodium softened make up water. The NORTH train has had a history of much higher iron contamination than either of the other two. It was agreed to conduct a study to determine a means of reducing this iron contamination to an acceptable level. This study has developed a chemical treatment program capable of a reduction of 92 percent.

INITIAL TREATMENT AND CONDITIONS

The condensate treatment program consisted of feeding an octadecylamine based filming amine at a level of 1 PPM into the condensate return water. The iron levels in the North Train varied between 3 and 6 PPM as Fe. The condensate pH varied between 4.2 and 5.9.

TREATMENT CHANGES

Because of the excessive amount of iron being returned to the 485 and 280 PSIG boilers, steps were suggested to dealkalize the makeup water

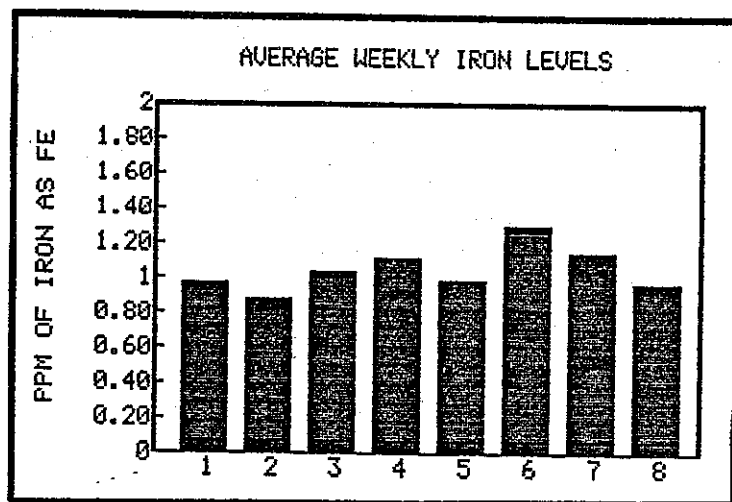
to reduce the source of carbon dioxide causing the very low pH conditions. The capital was not available and it was decided to attempt to elevate the pH to 6.5 to 7.0 by using a 50/50 blend of morpholine and cyclohexylamine plus 0.5 ppm of catalyzed hydrazine supplied as DREW AMERZINE®. The filming amine currently used was to be continued at the same level.

These materials were fed into the condensate at the evaporators. The data collected over the next three months revealed that the pH was increased to 6.0 to 6.3, but that efforts to reach the desired level would be excessively expensive. There was only a marginal improvement in the average iron level and with a variation between 2.5 and 4.3 PPM.

As the condensate is collected in an open storage tank, it was concluded that a large amount of the cyclohexylamine was being lost and not being recycled through the system. In an effort to minimize losses at the storage tank, the cyclohexylamine portion was replaced with morpholine. Concurrent with this change, hydrazine was increased to 1.0 PPM. The filming amine feed was as before.

The next two months did show some improvement but results were very erratic with the condensate iron levels varying between a low of 0.5 and a high of 3.7 PPM. The weekly averages based on daily tests for this period are shown in the figure below. The average iron level and pH for this period were 1.07 PPM and 6.7, respectively.

FIGURE A



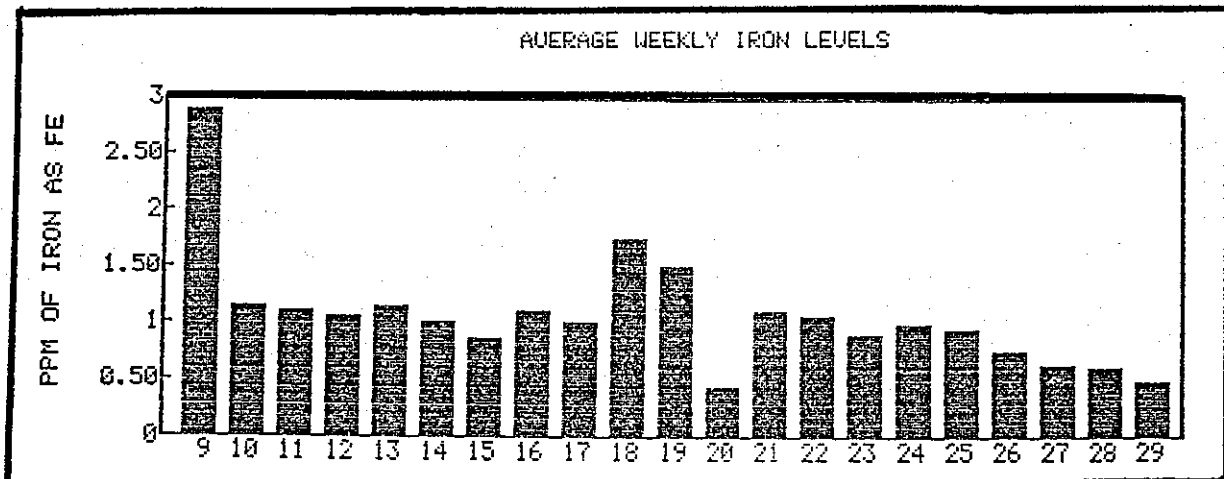
To further reduce possible amine losses, the feed point of the morpholine/hydrazine was relocated to the discharge of the open storage tank. No other changes were made. This change had virtually no effect, other than an initial one week peak of 2.9 PPM of iron, over the next 9 weeks.

At this time the filming amine was changed to 2 PPM of extoxylated amine supplied as DREW OF[®]. A "cleaning" was observed with an increase in the iron level over the next week reaching a peak of 1.76 PPM and it took the next three weeks to level off to the previous levels.

Without changing any materials or dosage levels, the feed point of the morpholine/hydrazine was changed to the steam supply lines. It should be noted that there are two such lines to the phosphoric acid evaporators. Initially the feed was split evenly between the two. Variations in feed to each line (using same total amount) revealed no correlation with test results. The results over the next four weeks showed another marginal improvement with the weekly averages being 0.96 PPM.

The filming amine was then increased to 4 PPM. Unlike the previous increase in filming amine, no "cleanup" was noted. Rather, the level of iron dropped to an average of less than 0.5 PPM by the end of the fifth week of this treatment. However, deposition in a turbine condenser developed and feed of the filming amine was completely aborted. Although the iron levels remained about the same over the next two weeks, an increase to about 2.0 PPM took place over the next thirteen weeks. The figure below shows the average iron levels from the end of the previous figure through the abortion of filming amine.

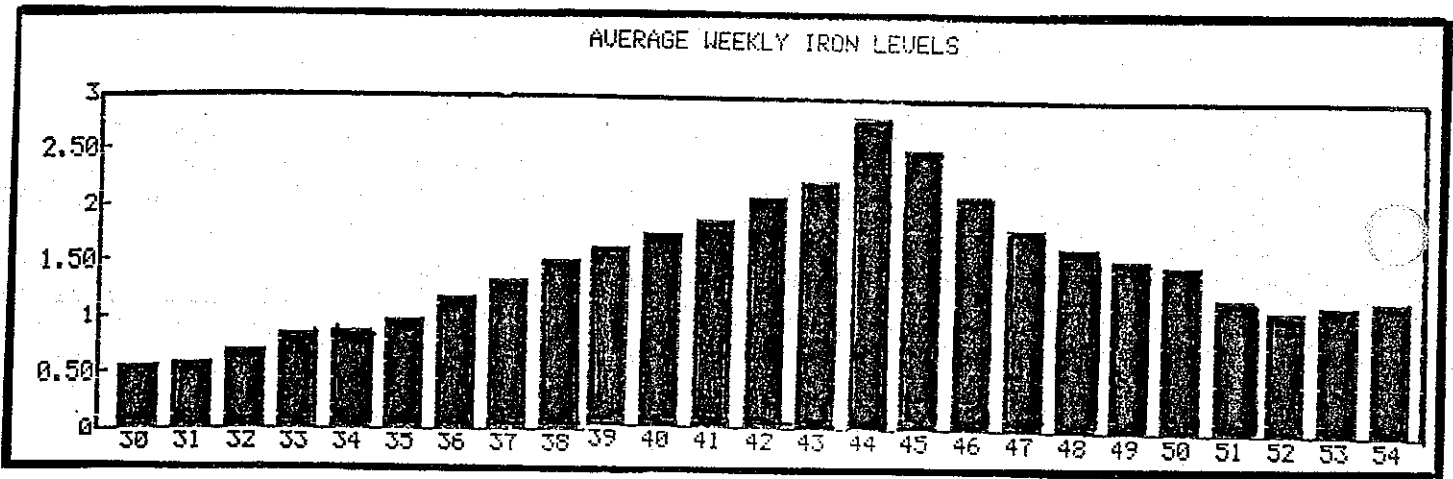
FIGURE B



It was apparent from the data collected to this point that the filming amine is essential to the program and thus it was restarted. However, it was only fed at 1 PPM as a safety precaution. Again a "cleanup" was seen with the iron increasing over the next two weeks to a peak of 2.8 PPM before slowly dropping over the next seven weeks to a level of about 1.2 PPM. It then remained at this level for three additional weeks. During all this period the pH was still generally in the range of 6.5 to 6.7. At this point the filming amine was increased to 2 PPM>

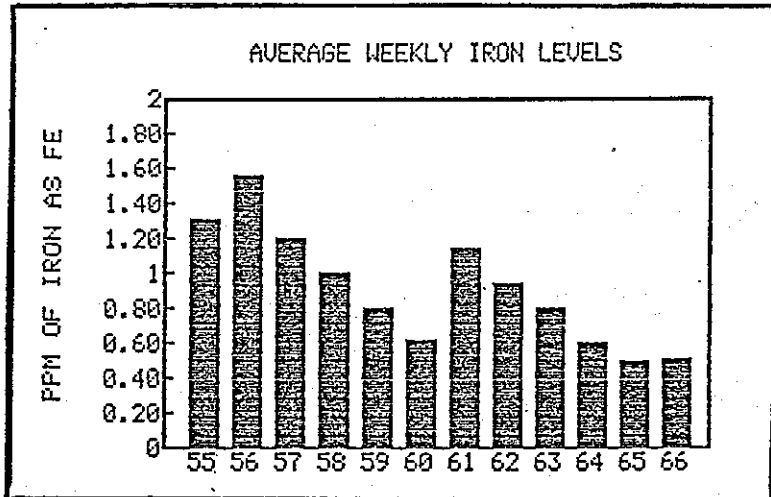
The figure below shows the average weekly iron levels covering the period from the end of FIGURE B up to the point of the 2 PPM of filming amine feed.

FIGURE C



Following the increase in filming amine to the 2 PPM level the iron increased initially to 1.56 PPM then decreased to about 0.6 PPM over the next six weeks. In an effort to increase the pH, a blended amine, DREWCOR 8750, replaced the morpholine, but at a lower dosage level. The results were that the pH dropped to about 5.8 to 6.2 with an increase in the iron to a weekly average of 1.15 PPM after the first week and then dropped to 0.8 after three more weeks. Since the pH was low, the neutralizing portion of the program was changed to a mixture of morpholine and the blended amine. During the last three weeks of this study using these conditions, the pH increased to about 6.3 to 6.6 and the iron levels dropped to an average of 0.5 PPM. The following figure illustrates the last portion of the study.

FIGURE "D"

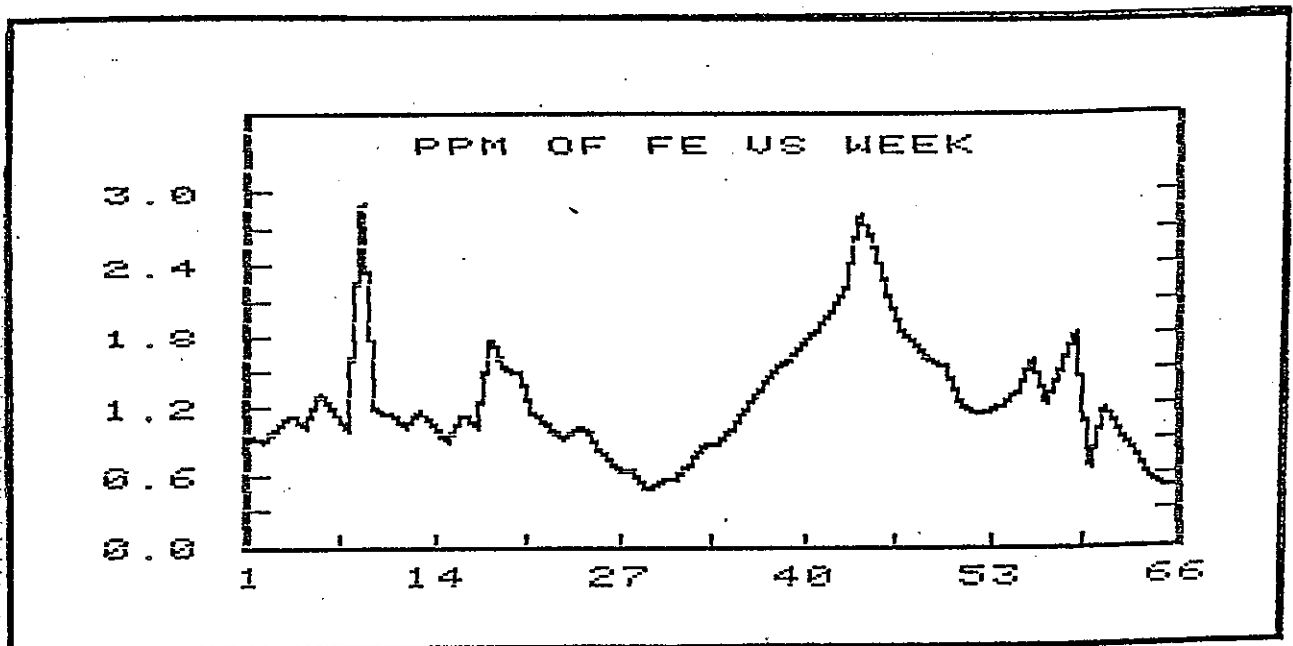


SUMMARY

The use of blended amines to adjust the pH, catalyzed hydrazine to scavenge dissolved oxygen and reduce metal oxides and filming amine to provide a corrosion barrier has reduced the weekly average iron levels in the North Train condensate from about 6 PPM down to approximately 0.5 PPM. This is a 92% reduction.

The figure below combines FIGURES A, B, C and D from above to give an over all view.

FIGURE E



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