1934

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Recommended Citation

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THE STUDY AND SOLUTION OF A CORROSION PROBLEM INDUCED BY AIR CONDITIONING.

by

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A
THESIS
submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY
OF MISSOURI
in partial fulfillment of the work required for the
DEGREE OF
CHEMICAL ENGINEER
Rolla, Missouri
1934

Approved by W.T. Schrenk.
Professor of Chemistry.

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INTRODUCTION

Engineers and architects are beginning to realize the full economic importance of air conditioning and are so designing modern buildings that this feature is always included as an integral part of the design.

A large industrial insurance company estimates that the time lost by employees due to colds and other respiratory diseases, induced by polluted air, is costing business and industry millions of dollars each year. This does not take into consideration the indirect losses resulting from reduced efficiency of executives and department heads caused by the absence of assistants, or the slowing up of production, the costly mistakes and unavoidable waste due to inexperienced men replacing key workers who are absent because of sickness.

A record of the air pollution in each school section, or ward, of the City of Akron, Ohio,[1] maintained over a period of two years, together with the number of school absentees and the total number of deaths has shown a remarkable relationship existing between these two

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[1] American Air Filter Company, Inc., Booklet, Filtered Air, Its Importance in Building Ventilation and Air Conditioning.

items. The results of this investigation are shown in Figure 1.

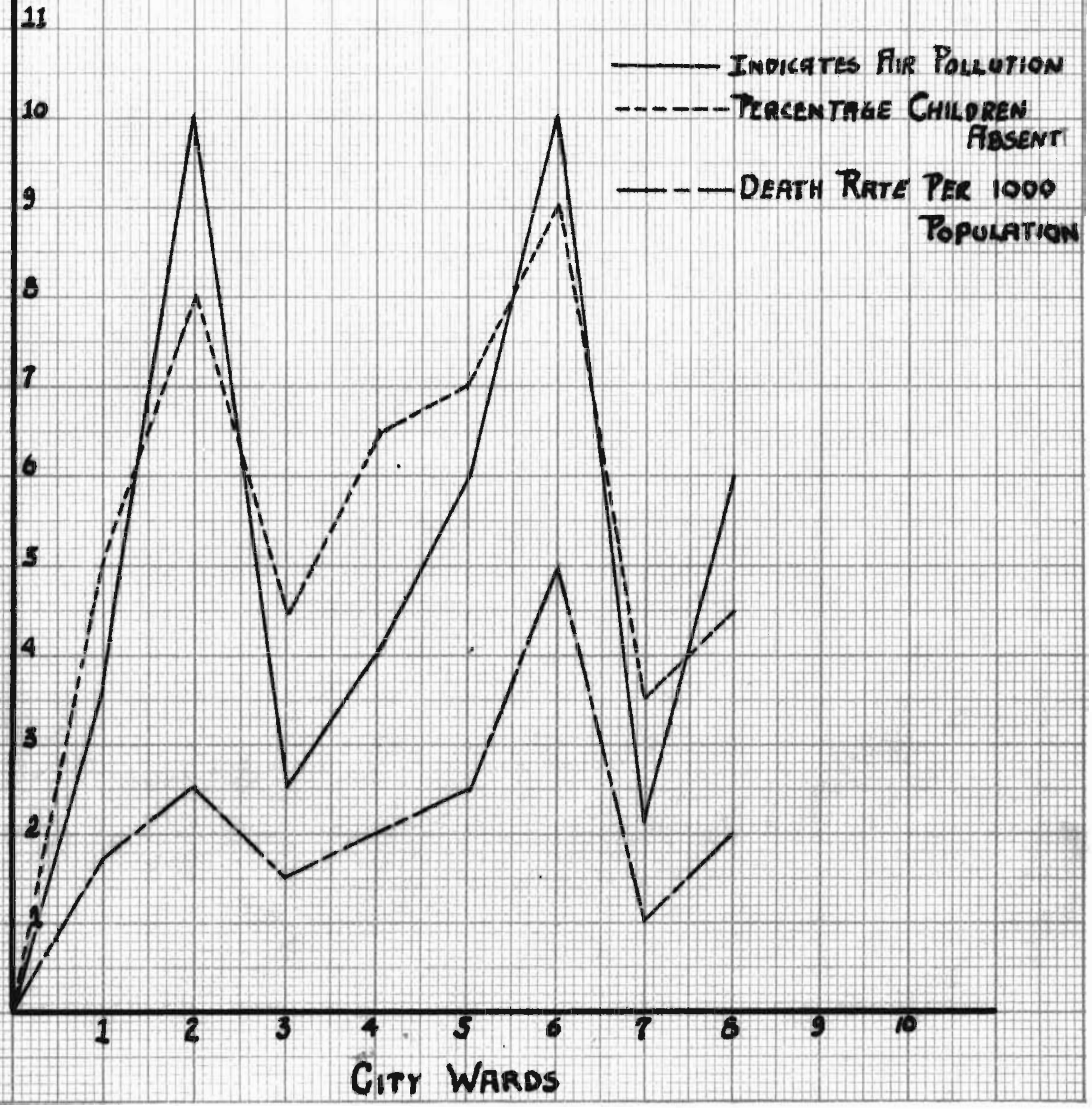
The United States Weather Bureau in cooperation with the Research Committee of the American Society of Heating and Ventilating Engineers, is conducting investigations in fourteen cities of the United States, in an endeavor to establish the exact relation of excessive air pollution to the abnormal prevalence of respiratory disorders. Results of these investigations will, without a doubt, exert a powerful influence on future building design, as regards provisions for air conditioning.

At the present time an Open Forum on Air Conditioning is being held in St. Louis at the David Ranken, Jr., School of Mechanical Trades. There will be a total of eight meetings, one held each week.

The purpose of this Forum is to acquaint the public with the value of air conditioning from the standpoint of health and comfort, to present the facts pretaining to the methods of accomplishment and to correct some public misconceptions that exist. The discussions are of vital interest alike to the engineer, architect and mechanic.

FIGURE 1

CITY OF AKRON, OHIO
RELATION OF AIR POLLUTION
TO
ABSENTEEISM AND DEATH RATE



The topics discussed include Air Cleansing and Washing, Engineering of Air Conditioning and their allied problems.

This Forum, attended by the writer, indicates the ever increasing trend to complete air conditioning installation in all new and modern buildings.

This definite trend is bringing the allied problem of corrosion to the foreground and will, without a doubt, create the need for chemical engineers skilled in the methods of combating corrosion.

Conditioned air is brought about by the use of air filters, air washers, dehumidifiers, reheaters, power fans and allied equipment such as water storage tanks, circulating pumps and piping systems.

A recent personal investigation conducted by the writer has disclosed the extremely interesting fact that almost every large air conditioning plant in operation in St. Louis is experiencing serious difficulty in operation due to corrosion of some component part.

With the ever increasing number of installations of large air conditioning plants the problem of corrosion prevention is becoming one of major economic importance.

THE PROBLEM OF THE GLOBE-DEMOCRAT PUBLISHING COMPANY

A case of complete failure of a component part of a large industrial air conditioning system was brought to light recently when the Globe-Democrat Publishing Company in St. Louis, Missouri, requested the firm of Robert W. Hunt Company, Engineers, to act as consultants and to make an investigation of the piping system recirculating spray wash water in the air washing unit of their air conditioning system. Recommendations were to be made regarding the necessary steps to be taken to prevent reoccurance of any abnormal conditions found. A new piping system, replacing the old, was to be installed and it was imperative that all conditions causing corrosion be eliminated.

The writer, employed at that time by the Robert W. Hunt Company as an engineer and Assistant to the Manager, was assigned to this problem, making the investigation, studying all data obtained, recommending certain changes and the maintaining at all times of certain conditions in the air washing system.

To date these recommendations have proven very satisfactory and the new system has not evidenced any sign of corrosion and none is anticipated in the future. The above investigation and preventive measures adopted form the basis of this thesis.

The Globe-Democrat's air conditioning system was designed by a prominent St. Louis consulting engineer, Mr. Jos. O. Osborne. This system was installed for the following specific reasons.

The uninterrupted and most efficient operation of large newspaper presses can best be done in an atmosphere of specific temperature and moisture content. Paper strength and the magnitude of the static charge on the press rollers are dependent upon temperature and humidity and therefore these two factors govern the speed at which the paper can be run through the presses without rupture. Rupture of the paper, of course, causes shut down of the presses which in turn delays publication of the paper, a serious economic matter.

The comfort of the pressmen was also considered as their comfort is a measure of their efficiency, which today is of vital economic importance, especially in newspaper work where no delay is tolerated.

The maintaining therefore, within comparatively narrow limits, of the temperature and relative humidity of the air in the press room especially, necessitated the installation of complete, electrically controlled, air conditioning system. The following shows the component parts of this system.

- Air Ducts with Opening and Closing Dampers.
- Continuous, Self Cleaning, Viscous Type Air Filter.
- Spray Type Air Washer.
- Eliminator Plate Setup.
- Reheating Coils.
- Fan Assembly.
- Spray Wash Water Recirculating Pumps, Piping System, etc.

A sectional diagram of the system is shown in Figure 2.

Primary installation of the complete unit was made in 1931 and uninterrupted service was given until the Fall of 1932, when the pipe line supplying the pumps recirculating the spray wash water from the storage supply tank to the spray nozzles, gave evidence of leakage. This leakage was quite unexpected since the original specifications called for genuine wrought iron pipe, which pipe, after the short length of time in the system

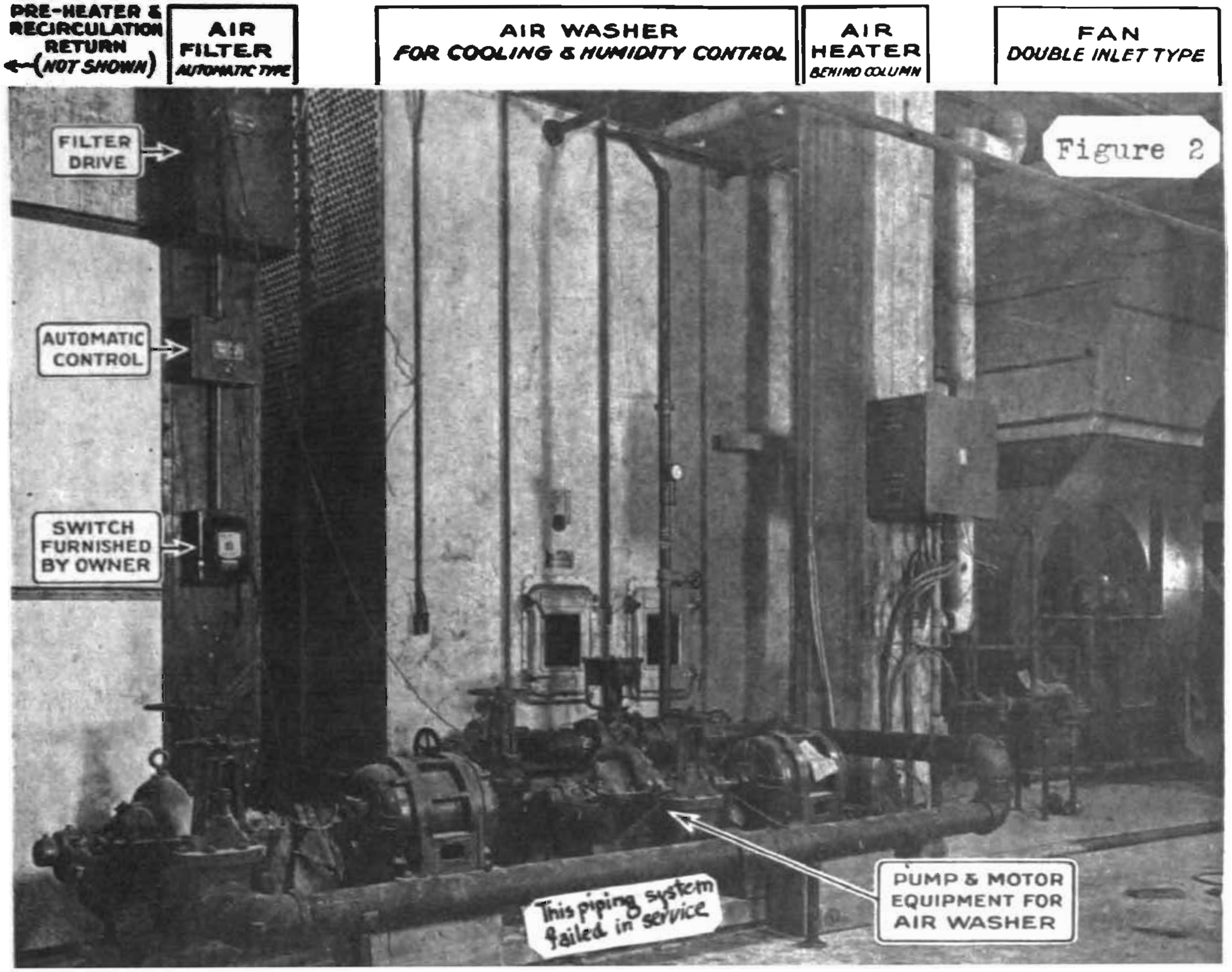


Figure 2

This piping system failed in service

certainly should not show failure if no abnormal conditions were present.

A preliminary investigation was immediately started and dealt only with the physical aspects of the piping system, pumps, and supply tank. This investigation disclosed that so complete was the failure of the piping system, due to corrosion, that complete reinstallation was necessary. This costly procedure plus the added losses due to conditions brought about by shut-down of the air conditioning unit made it imperative that a complete and thorough investigation be made to determine, if possible, all the underlying causes of corrosion and to take the necessary steps to prevent their reoccurance when the piping system had been replaced.

COMPLETE INVESTIGATION OF AIR CONDITIONING SYSTEM

The five inch diameter spray nozzle supply pipe was dismantled and visual examination disclosed the fact that the whole line was badly corroded, each individual section showing pitting, tuberculation and almost complete disintegration. From the lot of pipe an extremely corroded five inch nipple was chosen for chemical and microscopic analysis.

Figure 3 shows a photograph of a section of this pipe as it was removed from the original pipe line.

Deposits of corrosion products, secured from the water circulating line to the air washer, from the eliminator plates and sludge from the bottom of the air washer supply tank were subjected to chemical analysis.

Samples of water from various sources were secured, as well as samples of special preparations used in the system.

Samples of other materials were also taken for analysis, in order that the examination might be as complete as possible and show the causes of corrosion.

Examination of the supply tank itself revealed that the two primary coats of red lead in oil and a secondary coat of protective.enamel on this tank had so

Figure 3

protected it that no corrosion was evident.

The impellers on the pump shafts, the spray nozzles and attached fittings showed some slight evidence of corrosion, but not by any means as severe as that found in the piping system.

The following shows the results of various analysis made.

Miscroscopical Analysis of Corroded Nipple.

Two longitudinal sections taken from this nipple showed no carburized streaks and the slag and grain structure appeared normal.

Chemical Analysis of Corroded Nipple.

Percent	Carbon	0.027
	Manganese	0.031
	Phosphorous	0.131
	Sulphur	0.014
	Silicon	0.138
	Slag & Oxide	2.704

Chemical Analysis of Various Deposits.

The deposits, taken from locations as shown below, gave the following results on analysis.

(A) Deposit from circulating line to air washer.

(B) Deposit from Eliminator plate.

(C) Sludge from bottom of air washer storage tank.

Sample No.	(A)	(B)	(C)
Percent Silica	9.44	1.64	5.53
Iron, Fe.	39.37	6.18	58.74
Calcium Oxide	0.06	4.30	0.18
Magnesium Oxide	0.77	0.60	0.09
Sulphates, SO_3	29.30	32.60	5.30
Lead*	trace	35.60	4.00
Water Soluble	nil	nil	nil

*The high lead content of (B) is probably accounted for by the presence of lead oxide paint on the eliminator plates.

Chemical Analysis of Viscous Type Air Filter Liquid.

This liquid, an oil, was tested for total acidity, before and after use on the filter screen, with the following results.

Sample No.	Old Oil	New Oil
Total Acidity Mgms. KOH per Gram Sample.	0.04	0.03

Chemical Analysis of Printers Ink.

A test was made to determine the total acidity of the ink used on the presses with the following results.

Sample No.	Black Printers Ink
Total Acidity Mgms. KOH per Gram Sample.	0.55

Chemical Analysis of a Solution Sold Under Trade Name of "Rust Eradicator".

This solution had occasionally been used in the water supply system of the air washer. Results of analysis of this solution as follows:

Sample No.	"RUST ERADICATOR".
Percent Silica	25.80
Sodium Carbonate	5.06
Sodium Hydroxide	9.38

Chemical Analysis of St. Louis Water. (D)

Chemical Analysis of St. Louis Water with "Rust Eradicator" added. (E)

Chemical Analysis of Water From Air Washer System After a Full Period of Operation. (F)

The results of the three sets of analysis on water are as follows:

Sample No.	(D)	(E)	(F)
Temporary Hardness	2.55	2.09	--
Permanent Hardness	4.15	3.86	19.63
Free Acid, Terms H_2SO_4	--	--	1.83
Total Acid, " "	--	--	37.00
Total Dissolved Solids	15.07	13.05	55.59

Suspended Matter	0.20	0.13	0.38
Calcium Bicarbonate	2.55	2.09	--
Magnesium Bicarbonate	nil	nil	--
Calcium Sulfate	1.51	0.95	12.00
Magnesium Sulfate	3.65	3.80	10.30
Sodium Sulfate	5.19	4.12	23.80
Sodium Chloride	1.70	1.70	6.70
Iron and Alumina	0.07	0.08	--
Silica	0.40	0.31	1.83
	Grains per U.S. Gallon		
O_2 cc. per liter	--	5.60 5.90	6.23 6.09 6.00 6.60
Total Acidity, P. P. M. (Average of Four)		Alkaline	2.11
Hydrogen Ion Concentration	---	9.5	Less Than 5.0

Chemical Titration of Spray Wash Water in Use One Week, To Determine Amount of Sodium Hydroxide to Be Added To Secure a pH of 9-9.5

Indicator	Phenolphthalein
Hydrogen Ion Range	8.3-10.00
Titration Solution	Sodium Hydroxide
Concentration of Titrating Solution	20.00 Gms/L.

A 300 cc sample of water required 2.0 cc of the titrating solution to create a pH of 9.5.

The supply tank holds 1170 gallons.

The above nine series of analysis were made and results noted as shown. A careful study was then made of the theories of corrosion in order that the proper steps could be taken to prevent any reoccurrence of the trouble experienced in the operation of this air conditioning unit.

THEORY OF CORROSION

Iron, like all metals, has a definite inherent tendency to go into solution when placed in contact with water. Iron, however, can enter solution only by displacing some other element already in solution. For instance, a piece of iron placed in copper sulfate solution goes into solution, but at the same time copper is plated out and appears on the surface of the iron. In the ordinary case of iron immersed in water, hydrogen is the element plated out. This hydrogen gathers on the surface of the iron in the form of a thin, invisible film. The presence of this film tends to obstruct the progress of the reaction by insulating the metal from the solution.

In order that corrosion may proceed the film of hydrogen must be removed. This can happen in two ways: either it may combine with oxygen in solution to form water, or it may escape as gaseous hydrogen.

Dissolved oxygen is usually present in water solutions and removes the hydrogen film by reacting with it to form water. The process if then free to continue, that is to say, more iron can go into solution, more hydrogen can plate out and the process can continue at a rate determined by the speed with which the oxygen removes the hydrogen.

In acids the same reaction takes place. In addition to this, the tendency of the hydrogen to plate out is much greater, and so much of it gathers on the metal surface that it is forced off in the form of hydrogen gas bubbles. Corrosion, therefore, is proportionately more rapid in acid solutions than in ordinary neutral water.

CONSIDERATION OF THE MANY FACTORS WHICH INFLUENCE RATE OF CORROSION.

It is well known that the presence of oxygen is one of the most important of these factors. Other factors which have more or less influence on corrosion rate include metal potential (solution pressure) of the metallic iron, ferrous and ferric-ion contents of the water, hydrogen ion content of the water, contact of the metal with other conducting substances, chemical content of the corroding solution, existance of mechanical stress or strain in the metal and many others.

CLASSIFICATION OF FACTORS.

Primary Factors:

The factors that effect initial corrosion and determine the tendency for corrosion to proceed are termed primary factors, in the sense that they are present in the initial reactions in all cases of corrosion. These factors, which influence the corroding tendency only, are as follows:

1. As applying to anodic reactions.

Anodic reactions refer to the reactions which occur only at points which happen to be anodic.

The metal potential or the solution tendency of the iron, which is determined by,

(a) The normal potential of the metal.

(b) The concentration of the metal ions in the solution in contact with the metal surface. When acids, bases, or salts are dissolved in water to form dilute solutions, or electrolytes, some of their molecules are broken up or dissociated into atoms carrying electric charges. These charged atoms are called ions, those with a positive charge being cations and those with negative charges being anions. The positive and negative charges of the atoms, anions and cations, which go to make up a single molecule, are equal, and consequently, the molecule is electrically neutral. Metallic iron enters the solution as ionic iron, Fe^{++}.

2. As applying to cathodic reactions:

The potential available for the deposition and removal of hydrogen which is determined by:

(a) The hydrogen ion concentration (acidity) of the solution in contact with the metal surface.

(b) The normal potential of the hydrogen when it is being removed as gaseous hydrogen, and when it is being oxidized by oxygen in solution.

The above factors measure the tendency for corrosion, but other factors may be of far more practical importance in determining the corrosion which actually takes place.

EXPLANATION OF PRIMARY FACTORS.

1. Normal Potential of the metal.

Every metal has a certain tendency to go into solution with the formation of ions. This potential is the inherent force which sends metal ions into solution and thus initates and helps to maintain corrosion. The easiest way to measure this metal potential is to determine the opposing electrical potential which must be set up to prevent the metal from going into solution. By means of such measurements the metals have been arranged in the well known Electrochemical Series.

Ordinarly the most cathodic ions present in corroding solutions are those of hydrogen, and they are therefore, the easiest to plate out on the cathodic areas. The question whether a given metal will or will not go into solution and at the same time displace hydrogen, depends on its position in the Electrochemical Series as compared with hydrogen. Theoretically, iron will displace hydrogen ions from solution, even though they be present in very low concentration. It is primarily this tendency which accounts for the initial corrosion of iron in contact with water, especially when the hydrogen ion concentration is high, as in acid solutions. This conception is in itself sufficient to explain the tendency for pure iron to corrode, and does not require the presence of potential differences which result from impurities on the metal surface, or from contact with dissimilar materials, although it has been claimed by some investigators that these are necessary.

2. The hydrogen ion concentration of the solution in contact with the metal surface.

> The presence of hydrogen ions in high concentration makes the deposition of atomic hydrogen easy, and hence the tendency of iron to corrode is increased by increasing the acidity of the solution.

CORROSION REACTIONS, ELECTROCHEMICAL THEORY.

The initial corrosion reaction can be stated as follows:

Reaction 1:

$$\text{FE, metal} + 2\,H^{+}_{,}\ \text{ionic} = Fe^{++}_{,}\ \text{ionic} + 2\,H\ \text{atomic.}$$

W. R. Whitney[1] comments as follows in this connection. "Hydrogen acts as a metal and is electrolytically classified in the group with copper when compared with iron and zinc. That is, if a cell were made up on the Daniel model, iron being used instead of zinc, and hydrogen instead of copper, this cell would generate current when the hydrogen and iron electrodes were connected. Iron would then dissolve with a velocity dependent on the total resistance of the circuit. So, also, and for the same reason, iron when

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[1] Whitney, W.R., The Corrosion of Iron, J. Am. Chem. Soc., Vol. 25. pp. 394-406, 1903.

placed in a solution containing hydrogen ions will dissolve as the hydrogen precipitates, just exactly as when placed in the copper sulfate solution. That iron does oxidize or dissolve in all solutions containing appreciable quantities of hydrogen ions is well known. This electrochemical relationship between iron and hydrogen is the primal cause of rusting."

Although Whitney correctly stated the primary cause of corrosion, it was amplified by W. H. Walker[1] who demonstrated that there was another reaction, equally important if corrosion was to continue, this reaction showing how the polarizing or insulating film of hydrogen deposited on the surface of the metal was removed. This reaction can be stated as follows:

Reaction 2:

(a) 2 H, atomic $+ \frac{1}{2}O_2$, dissolved,
$=$ H_2O, liquid water.

(b) 2 H, atomic $=$ 2 H, molecular

Investigations by the Massachusetts Institute of Technology and the National Tube Company laboratories and results of practical observation, indicate that the

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[1] Walker, W. H.; Cederholm, Anna; Bent, L. N.; Corrosion of Iron and Steel. J. Am. Chem. Soc., Vol. 29, pp. 1215-1264, 1907. and Vol. 30, pp. 473-474, 1908.

amount of molecular, gaseous hydrogen produced by the corrosion of iron in neutral or alkaline water is very small compared with the amount of hydrogen removed by oxidation.

It is evident then that under these conditions the oxidation of hydrogen must account for Reaction No. 2, and govern the rate of corrosion.

Classification of all experimental data gathered in the past few years has shown that the whole field of corrosion of iron by dilute aqueous solutions may be divided into three main zones of varying hydrogen ion concentration. The following table shows principal factors arranged in approximately their order of importance in the three zones, each zone with a different pH range.

"Relative Influence of Important Factors on Corrosion of Steel Immersed in Water."

Alkaline Zone	Neutral Zone
Corrosion Slow	Corrosion Medium
pH greater than 10	pH of 4.3 to 10
1. Protective Coatings	1. Oxygen Concentration
2. Oxygen Concentration	2. Protective Coating
3. Composition of Metal*	3. Hydrogen Ion Concentration
4. Hydrogen ion Concentration	4. Composition of Metal*

Acid Zone

Corrosion Rapid

pH less than 4.3

1. Hydrogen Ion Concentration
2. Composition of Metal
3. Oxygen Concentration
4. Protective Coating*

The above factors are classified according to pH value and arranged in decreasing order of importance. Those marked * are of minor importance in their respective zones.

The order of importance of the above factors may vary as conditions change. For instance, in dilute acids, if the solution is air agitated, oxygen concentration may become a factor of first importance.

The neutral zone includes all solutions with ordinary oxygen concentrations at room temperature, and with pH values within the limits of about 10, where alkalinity is caused by NaOH and 4.3, where acidity is caused by HCl, and therefore covers many corrosion problems.

The acid limit is determined by total acidity rather than by hydrogen ion concentration. Thus, as pointed out by Whitman, a carbonic acid solution gives a certain amount of acid corrosion at about the total acidity as does an HCl solution, but in the case of the carbonic acid solution the pH is only about 5.5 against 4.3 for an HCl solution, since the carbonic acid is only slightly dissociated into hydrogen ions.

Furthermore, at low dissolved oxygen concentrations hydrogen gas is evolved from solutions of less acidity than at high concentrations. In the absence of oxygen, hydrogen gas can be slowly evolved even from neutral solutions. J. W. Shipley and I. R. McHaffie[1] have found that hydrogen gas is evolved at room temperature from alkaline water, in the absence of oxygen, with a pH of 9.4.

The limits of the neutral zone vary according to many conditions. The dominent factor in this zone is Reaction 2a, because, unless this reaction can proceed, the retention of the polarizing hydrogen film on the surface of the metal forces Reaction 1 to cease. The rate of diffusion of the dissolved oxygen to the metallic surface undoubtedly determines the rate of corrosion as

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[1] Shipley, J.W., McHaffie, I.R., Clare, N.D., Corrosion of Iron in Absence of Oxygen. Ind. Eng. Chem. Vol. 17, pp. 381-385, 1925.

it is the slowest factor in Reaction 2a.

From this it can be seen that air agitation of the corroding solution causes a very rapid corrosion rate, since it accelerates the rate which the dissolved oxygen reaches the metallic surface.

The thickness of the rust coating and its character, or any natural or artificial coating, which may be formed or have been applied on the surface of the metal, has a decided influence in this zone.

At normal temperatures, small variations in acidity or alkalinity of the water, as long as they are within the limits of this zone, have little effect on the corrosion rate in the absence of protective coatings because the solution next to the metal is maintained at a slight alkalinity by the solubility of ferrous hydroxide. The addition of certain salts effects the protective properties of the rust coating and in high concentrations they effect the oxygen solubility, Hence they exert a controlling influence on the ultimate rate of corrosion. The purity of the iron, within comparatively wide limits, has a negligible effect on the total amount of corrosion in this zone, as it does not effect Reaction 2a.

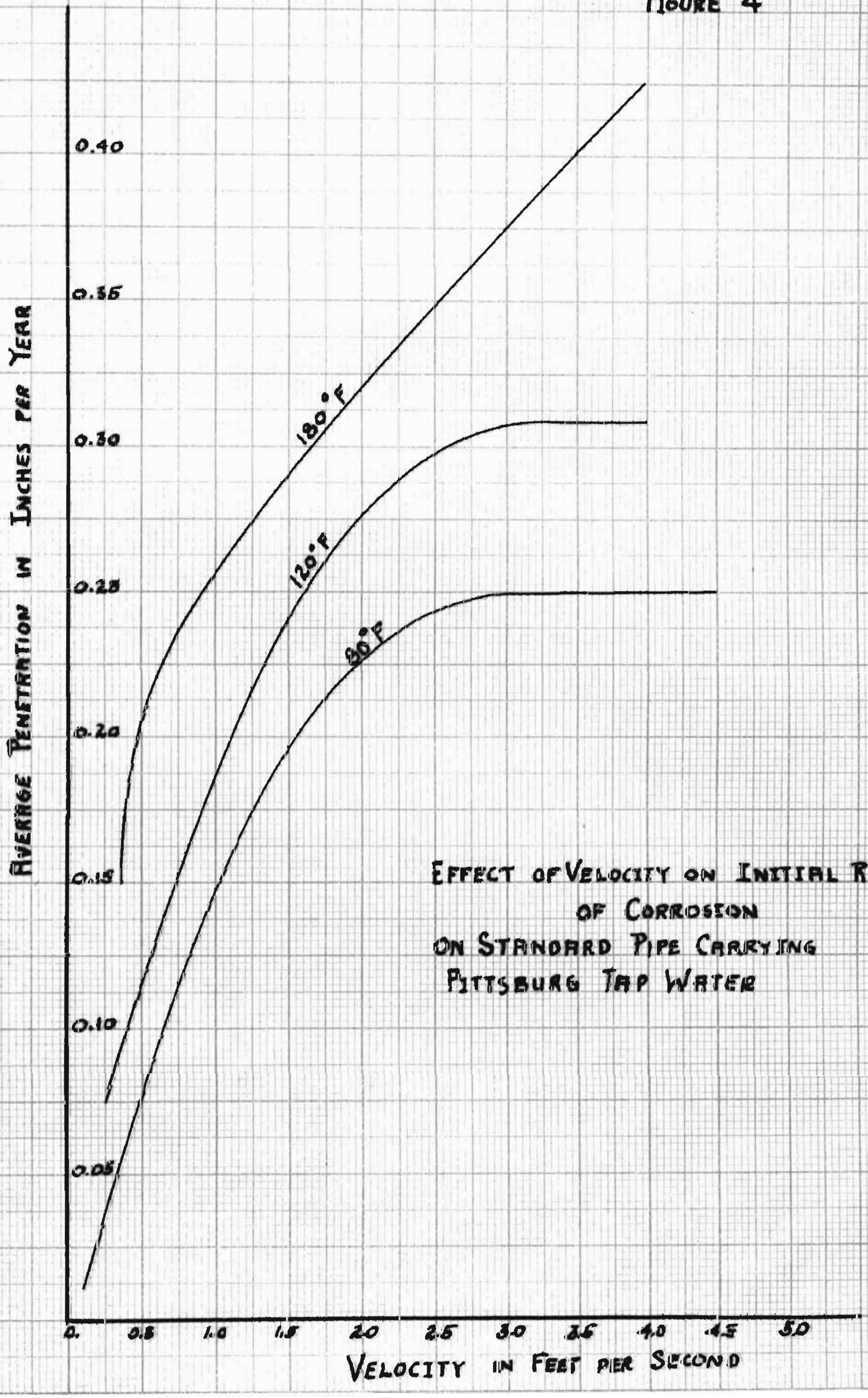
In the alkaline zone the alkalinity increases, and the concentration of the hydrogen ions decreases.

It might be assumed that the reduction of the hydrogen ions would become so great that Reaction 1 would be slowed down until it became the controlling factor or was stopped altogether. However, experimental data and theory has found that the hydrogen ion concentration may be greatly decreased, as in an alkaline solution, but that even under these conditions Reaction 1 is more rapid than Reaction 2a, which still limits the rate of corrosion. The true fact that an increase in the alkalinity causes a decrease in corrosion seems best accounted for by the fact that the rust coating formed, rather than the decrease in hydrogen ion concentration causes this condition. The rust coating formed in an alkaline solution is more protective than one formed in neutral solution, and hence the lower rate of corrosion.

In the acid zone the formation of molecular hydrogen gas from the nascent or atomic hydrogen is the most important reaction. Velocity of motion and temperature have a considerable influence on reactions in this range. If the velocity is greatly increased, oxygen depolarization may still be a major factor in non-oxidizing acids at normal temperature even in more concentrated solutions. Figure 4 indicates the effect of velocity on initial rate of corrosion.

The foregoing Electrochemical Theory, now the

FIGURE 4



EFFECT OF VELOCITY ON INITIAL RATE OF CORROSION ON STANDARD PIPE CARRYING PITTSBURG TAP WATER one most generally accepted, has superceeded the Acid Theory, Colloidal Theory, Film Theory, Biological Theory and the Theory of Direct Chemical Attack by Oxygen.

During the past twenty years the Electrochemical Theory has been considerably broadened in detail and may now be said to be accepted generally in explanation of the fundamental reactions and factors of corrosion.

CONCLUSIONS DRAWN FROM ANALYTICAL DATA OBTAINED

Under the chapter on "Complete Investigation of Air Conditioning System", we enumerate nine main examinations, stating the facts found, In this chapter we shall state the conclusions drawn from the results of the above mentioned examinations.

Microscopical Analysis of Corroded Nipple and Chemical Analysis of Corroded Nipple.

The chemical analysis and results of microscopical examination indicate that the nipple was high quality wrought iron. This finding is in keeping with specifications and also indicates no inherent defect in the metal was the cause of failure.

Chemical Examination of Various Deposits.

The conclusions drawn from this analysis confirm the opinion that the corrosive activity in the air conditioning system is due to acid constituents of the circulating water.

Chemical Analysis of Viscous Type Air Filter Liquid.

It was noted that both the samples of fluid from the air filter screen show a low total acidity, in fact the total acidity as revealed by the analysis is within the limits of the total acidity encountered with highly refined grades of mineral oils, such as are used for turbine lubrication and for electrical insulation. For this reason it was not thought necessary to consider this liquid as a possible contributary source for acid contamination of the spray wash water.

Chemical Analysis of Printers Ink.

The total acid content of this ink may be considered high and as the ink is a suspension of carbon in crude oil, the crude oil naturally carries certain sulphur compounds. Thus it is altogether possible, and we believed reasonably certain, that the printers ink which gained entrance into the air conditioning system was to some extent a contributing factor to the acid contamination found in the spray wash water.

Since this ink carried a high total acidity, which is undoubtedly mostly organic acidity, and since it also contains sulphur or sulphur compounds, it was the opinion that there was generated a certain amount of mineral acids, involving the above mentioned constituents, atmospheric dust, and moisture, so that due to oxidation and sulphonation, some mineral acidity resulted.

Chemical Analysis of the Solution, "Rust Eradicator."

Analysis of this compound indicated that it was mainly a solution of sodium silicate with sodium hydroxide. The use of this chemical was perfectly safe and advantageous. However, it had not been properly used and therefore had little beneficial effect on the system.

Chemical Examination of the Three Water Samples, Marked in the Report as (D), (E), and (F).

The analysis of the city water, with and without treatment, indicated a quality such that no failure of the character encountered would result through its use alone, with no other influences present. The analysis of city water reveals somewhat more than two grains of carbonate, therefore with no contamination of the water supply a precipitation of protective film in the supply lines would be expected.

The concentrated water from the air washing system was expected to reveal some increase in carbonate over that of city water. Such conditions would naturally obviate corrosion due to acid constituents in the water.

The analysis of the sample of water from the air washer system indicated quite clearly that acid contamination due to both mineral and carbonic acid was resulting in the air conditioning system. It is to be noted that the analysis shows approximately 1.8 grains per gallon free mineral acid with a total acidity of 37 grains, both in terms of sulphuric acid. Correcting the total acidity for free acidity plus the permanent hardness, leaves approximately 16 grains, which is undoubtedly carbon dioxide.

A comparison of the sodium chloride content of the city water after the treatment addition, with the same constituents in the water from the air washing system, indicated that the water from the later source had been concentrated to unit volume 3.90 times. A comparison of the total dissolved solids in the afore mentioned two samples indicated the water from the air washer system had been concentrated to unit volume 4.25 times. This shows an increase in total dissolved solids in the water from the air washer system.

The ratio of total sulfates to sodium chloride in the city water sample after the addition of "Rust Eradicator" is approximately 5. The ratio of the same constituents in the sample from the air washer is approximately 8, which indicated an increase in the total sulfates in the concentrated water from the air washer. This, of course, is in agreement with the comparison cited above, which indicated an increase in the total dissolved solids in the concentrated water from the air washer. From the data thus far, the conclusion was drawn that the acid contamination and concentration which was encountered in the concentrated water in the air washer system was due to a pick-up of SO_2 fumes with subsequent possible oxidation to SO_3 and carbon dioxide.

For a considerable length of time before failure of the system occured a large construction project was in progress adjacent to the Globe-Democrat building, and steam shovels kept the air filled with smoke and fumes. The intake of the outside air supply of the Globe-Democrat took in much of this smoke and fume, which undoubtedly contributed greatly to the sulfuric anhydride content of the water in the air washer.

The atmosphere then seemed to be the logical source of water contamination.

The fact that the air is circulated and recirculated to the conditioning plant led us to believe that this was the main contributing source of carbon dioxide contamination. Even though the high carbon dioxide content was present, it was quite probable that any free mineral acid, catalyzed and aided by carbon dioxide, was probably the most active constituent with respect to corrosive failure.

The amount of free carbon dioxide in excess, present over and above the concentration necessary, in equilibrium with bicarbonate ions, to keep the calcium present from separating out as calcium carbonate, is called aggressive carbon dioxide. This aggressiveness, or non-aggressiveness is therefore only directly applicable to calcium carbonate. Indirectly, however, it has this most important bearing on the behavior of water in contact with metallic surface, then when the carbon dioxide concentration lies below the aggressive point, the water will tend to deposit a protective coating of calcium carbonate; while, where it is over the aggressive point, the protective layer will be dissolved and the metal will be left open to attack.

Experiments by Bosshard and Pfenniger[1] are fairly conclusive that in the absence of oxygen, carbonic acid and electrolyte, corrosion is greatly restricted; that hydroxyl ions, as is now well understood, exert a powerful protective influence; and that the commonly occuring ions Mg and Cl seem the least desirable.

Figure 5 shows the effect of CO_2 concentration on the corrosion of steel.

The dissolved compound usually found in water which produced Mg and Cl ions is magnesium chloride. This substance is supposed to react with the water with the resulting production of magnesium hydroxide and hydrochloric acid. This usually occurs at elevated temperatures, as in a boiler at the surface of a steam bubble, just where it is disengaging itself from the metal: - the hydrochloric acid that is liberated (and which is fairly concentrated in the immediate vicinity of the point of liberation) reacting with the iron of the boiler to form iron chloride. This means that the boiler loses a certain amount of metallic iron, a loss which evidences itself as pitting,

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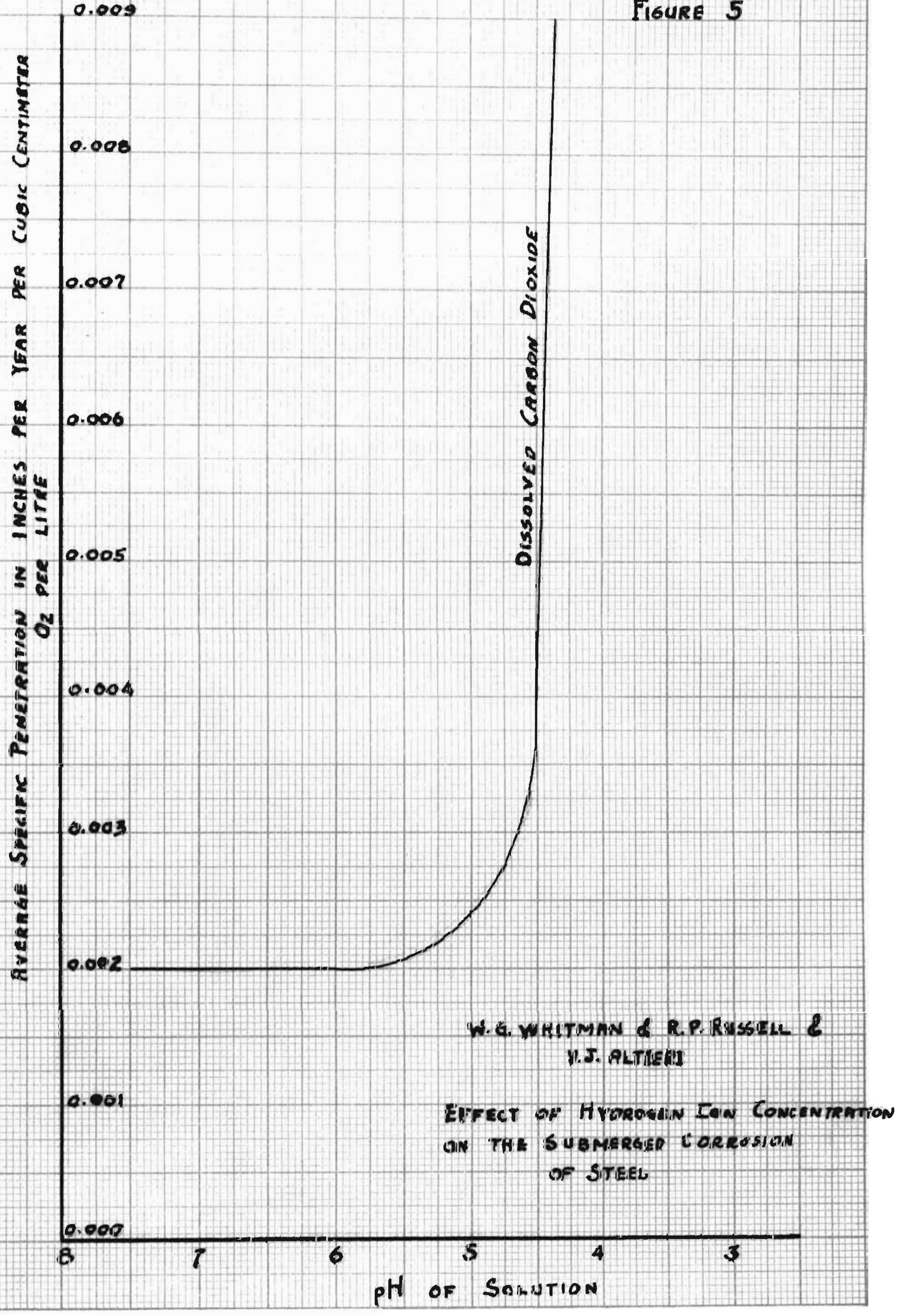
[1] Bosshard, W.; Pfenniger, K. Chem. Zeit. Vol. 46 pp. 5-6; 46-48; 63-64; 91-92; 1916.

FIGURE 5



W. G. WHITMAN & R. P. RUSSELL &
V. J. ALTIERI

EFFECT OF HYDROGEN ION CONCENTRATION
ON THE SUBMERGED CORROSION
OF STEEL

or corrosion. The iron chloride that is formed is in its turn decomposed by heat, giving finally one or more of the iron oxides and hydrochloric acid. The hydrochloric acid thus set free again combines with the magnesium hydroxide to form magnesium chloride, and the process repeats.

Other salts or combination of salts (such as magnesium sulfate, magnesium carbonate, nitrate and ammonium chloride) may cause or accelerate subaqueous corrosion, but magnesium chloride is probably the most notable offender of this type.

METHODS APPLIED TO INHIBIT CORROSION

A thorough study of the whole problem, and using as a basis the chemical analysis and conclusions and the theories of corrosion, led the writer to the conclusion that the most economical and surest method of inhibiting corrosion to the greatest degree was the maintaining in the water system of free hydroxyl ions in such concentrations that the pH of the water would always remain at a value of 9.0 to 9.5.

Figure 6 shows the relationship of hydrogen ion concentration on the corrosion of steel.

Figure 6A shows the percentage of soluble iron existing in solutions of various pH concentrations. See Baylis, J.R. in bibliography.

Sodium hydroxide seemed the most logical chemical to use as a source of hydroxyl ions, since it is one of the strongest and most highly ionizable bases we have, and can be purchased at such a nominal cost. Therefore, this chemical was chosen for use in the Globe-Democrat water system.

The maintenance of an hydroxyl alkalinity in such concentration that the pH will be 9.0 to 9.5 will tend to cause the small amount of calcium carbonate in the city water to precipitate and to remain as a thin

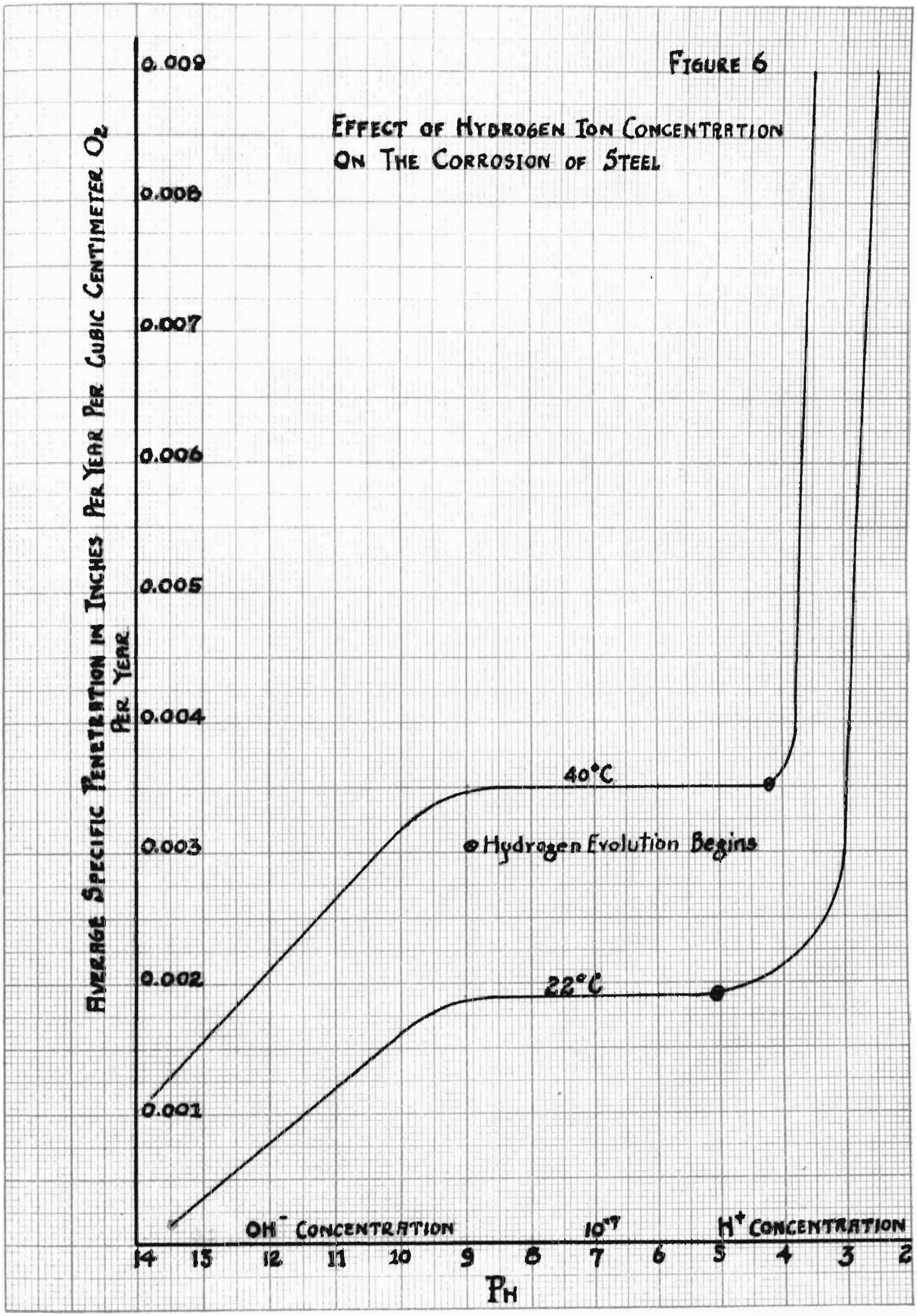
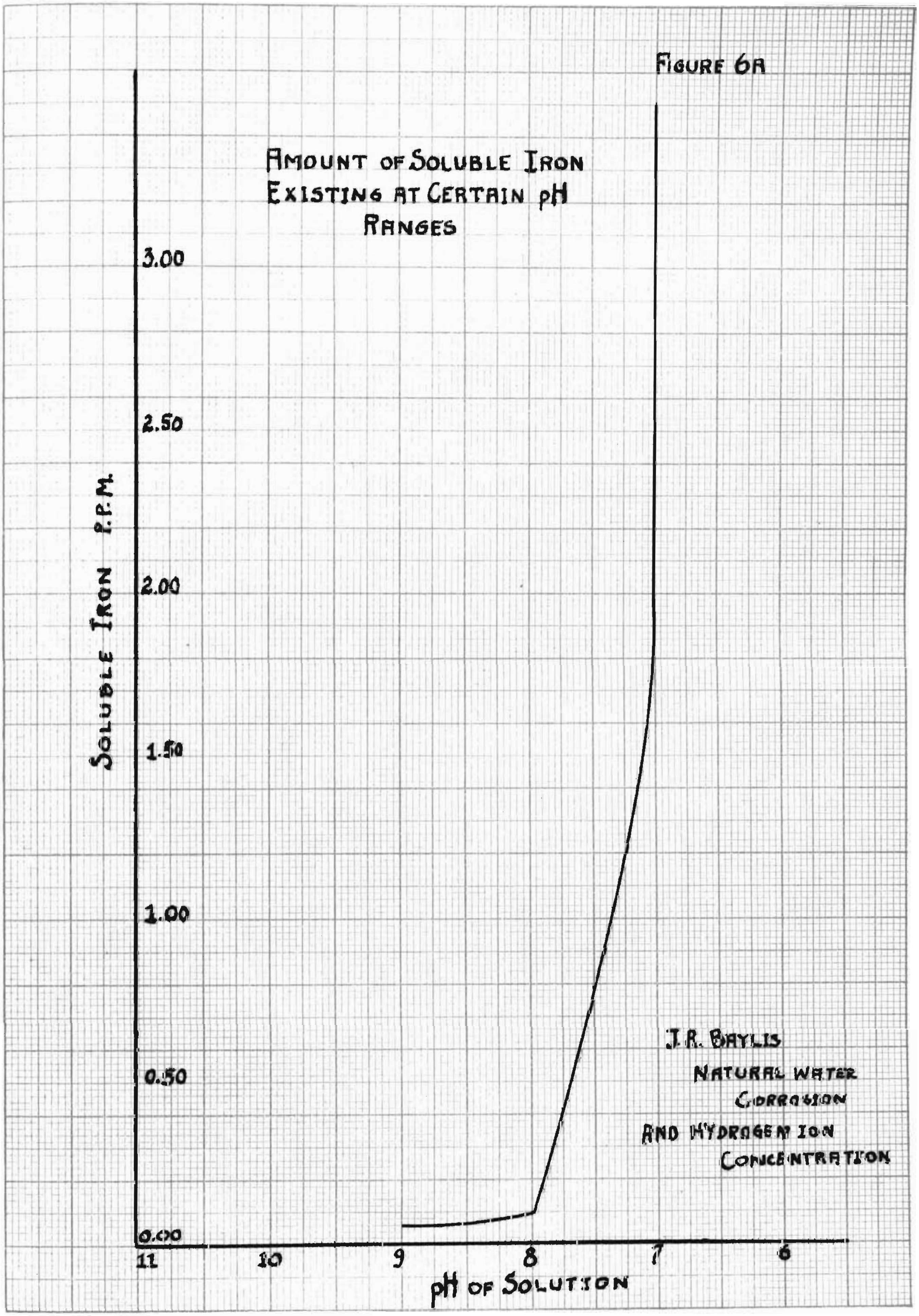


FIGURE 6

EFFECT OF HYDROGEN ION CONCENTRATION ON THE CORROSION OF STEEL

FIGURE 6A



AMOUNT OF SOLUBLE IRON EXISTING AT CERTAIN pH RANGES

J.R. BAYLIS
NATURAL WATER CORROSION AND HYDROGEN ION CONCENTRATION

protective coating on the inside of the supply pipe.

Some thought was given to the administering of about two pounds of lime to the storage tank each time it was filled with a fresh charge of city water, once weekly, but this was not advocated as it was later decided that the amount of calcium carbonate in the city water would in itself give a sufficiently ample protective coating in time if the pH would be maintained at 9.0 to 9.5.

When the presses were running, etc., the contamination of the spray wash water would be greatest and consequently at that time a reserve of OH ions should be present to act as inhibitors and neutralizers of acid contamination. This fact caused a careful study of press operations to be made with a check in the amount of pH change in the wash water during this period.

The results of a series of actual tests showed that after a twenty-four hour run, initial pH of 9.5, the water in the air washer storage tank required an average of 13 ounces of sodium hydroxide to bring the pH back to the initial 9.5.

The nozzles in the air washer spray 900 gallons of water per minute from a supply tank having a capacity of 1170 gallons of water and this 900 gallons of sprayed water washes 80,000 cubic feet of air each minute. This gives an approximate figure of 90 cubic feet of air washed per minute per gallon of water. A twenty-four hour run means 129,600 cubic feet of air washed by the recirculation of the same 1,170 gallons of water. This amount of air so altered the water that it required thirteen ounces of sodium hydroxide per 1,170 gallons of water to bring back the pH to 9.5. This figured that every 9,970 or approximately 10,000 cubic feet of air so altered 1,170 gallons of recirculated water that it required one ounce of sodium hydroxide to neutralize acid contamination and to bring back to initial pH of 9.5. This means that the washing of 10,000 feet of air at this plant imparts approximately 1.55 ounces of carbonic acid to the water in the storage tank.

In order that the correct amount of sodium hydroxide be added, and to insure a more or less constant pH, a chemical feeder of the batcher type was installed on the main water supply pipe supplying both circulating pumps. This feeder was equipped with a gauge glass which had been carefully calibrated and so marked that certain definite increments of its charge could be added to the supply line as they were needed.

From the study of press operation, etc., the following schedule was finally selected as the one best suited to meet existing conditions. This schedule is as follows:

EACH DAY

Corrective Solution to be added at 10:00 P.M.
" " " " " " 4:00 A.M.
" " " " " " 10:00 A.M.
" " " " " " 4:00 P.M.

The above schedule has been faithfully adhered to and, to date, all evidence indicates that corrosion in this air conditioning plant has been completely inhibited and this unit has since given satisfactory and uninterrupted service.

The photograph, Figure 8, shows the air conditioning unit of the Globe-Democrat Publishing Company.

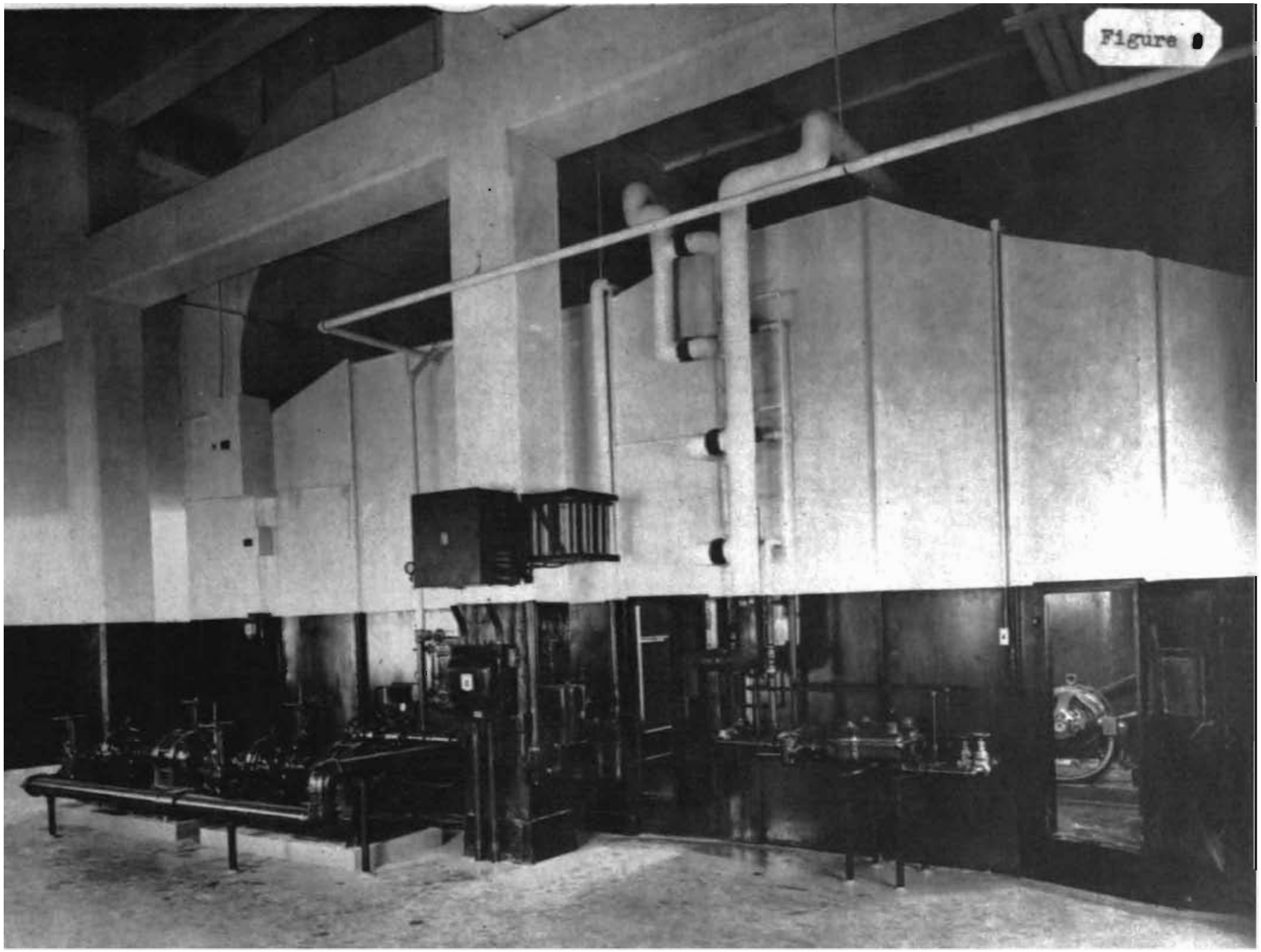


Figure [illegible]

SUMMARY

The foregoing is an outline of the method of attacking this corrosion problem, showing the investigations made, the resulting data obtained, the conclusions drawn and the corrective measures applied.

Considerable thought was given to the theory of corrosion and its application to this particular problem. After all factors involved had been given careful consideration, a certain definite corrective treatment was decided upon and this treatment called for the constant maintenance of the circulating water at a pH of 9 to 9.5.

To insure this condition a graduated chemical feeder was installed in the recirculating spray wash water line. At certain predetermined times an increment of the chemical contents of this feeder was permitted to enter the spray water system.

A careful study of press operation time was made which study indicated the proper time to add corrective chemical to the water system.

The amount of chemical added each set time was calculated in the laboratory, as outlined in Chapter 3.

If all conditions under which this air-conditioning system operated would have been constant, the prescribed treatment of the addition of a certain weight of corrective chemical at the stated time intervals would have been sufficiently accurate to insure a practicably constant pH of 9 to 9.5.

However changing atmospheric conditions, etc., introduced certain variable factors which factors might so alter the air being conditioned that the prescribed treatment would be over or under in quantity, with a resulting pH of the spray wash water out of the set limits.

Because of the above possible variations a check every four hours of the pH value of the spray wash water was advocated. For this purpose, after a study of the various hydrogen ion determining apparatus available, a Hellige, Hydrogen Ion Comparator, Block Type, was purchased. This Comparator was equipped with a Color Standard Disc Calibrated to read pH values of 8.4 to 10.2 in 0.20 intervals.

This type of Comparator was chosen because it was an inexpensive outfit and extremely simple to operate. It could, therefore, be placed in the hands of an inexperienced plant operator and after a small amount of instruction this operator could usually be depended upon to make correct determinations of the pH value of the water tested.

After adding the definite amount of corrective chemical at the set time the operator of the air conditioning unit now checks the pH of the water and if it is low he adds additional chemical until the pH is 9 to 9.5.

To date, however, the system has been running remarkably uniform and the originally prescribed amount of chemical administered at the calculated time has proven ample to take care of all variations that have been evidenced.

Recent examination of the whole system by Globe-Democrat Engineers revealed that practically no corrosion has occurred in the new system and none is expected.

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