THE EFFECT OF DISSOLVED OXYGEN ON THE

CORROSION OF COPPER BY HIGH VELOCITY

WATER

by

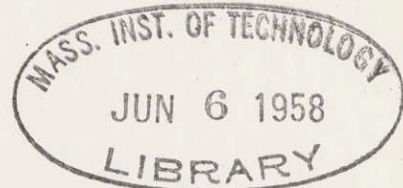RONALD G. HADGE   DENNIS C. REVELOTIS

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h
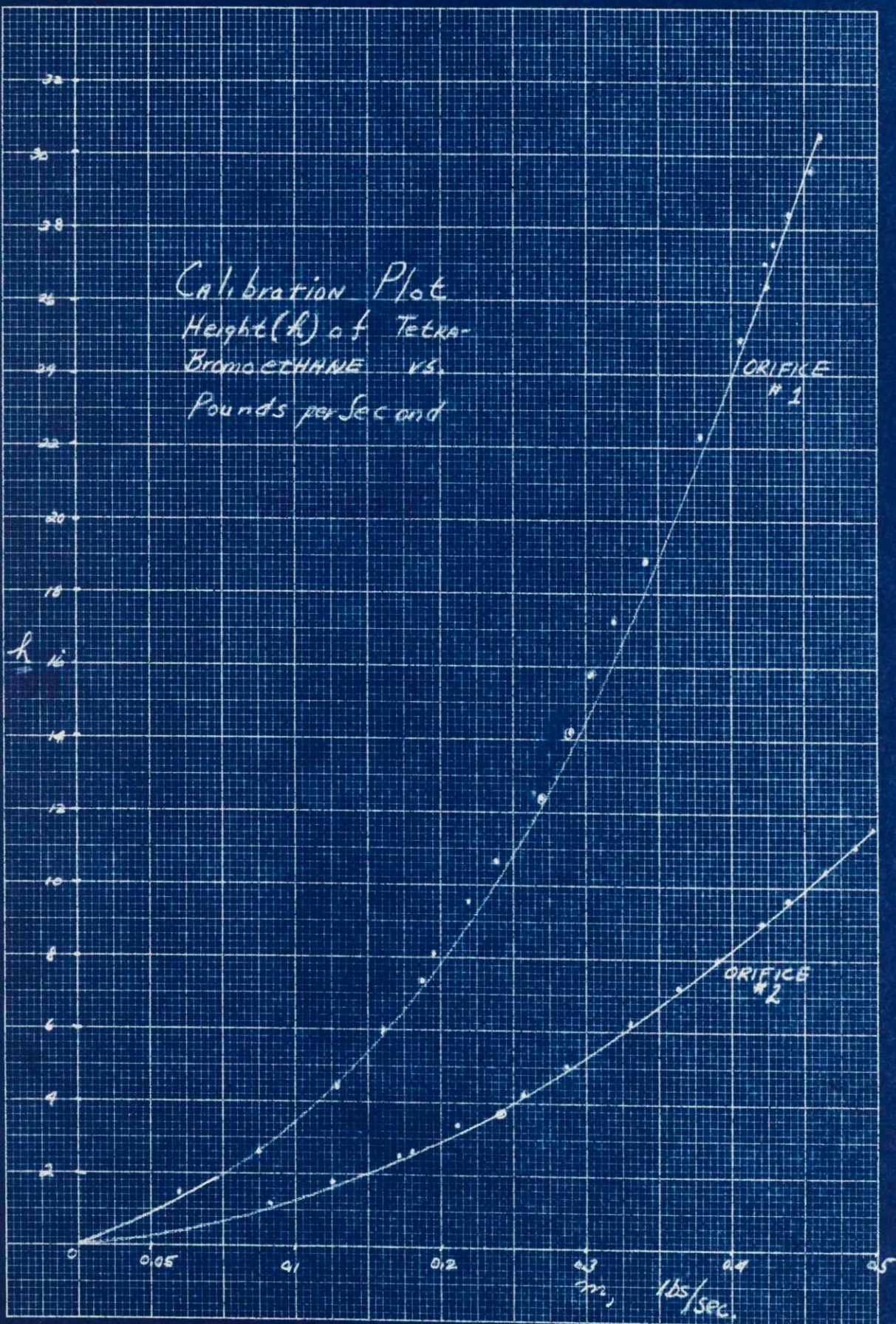
Calibration of Fisher Photoeletrometer
For Cu# Detemination

Percent of Light Transmitted

650 mµ Filter
3% NaCl

525 mµ Filter
Distilled Water

40

30

20

10

0

0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09

Cu# Concentration, P.P.M.
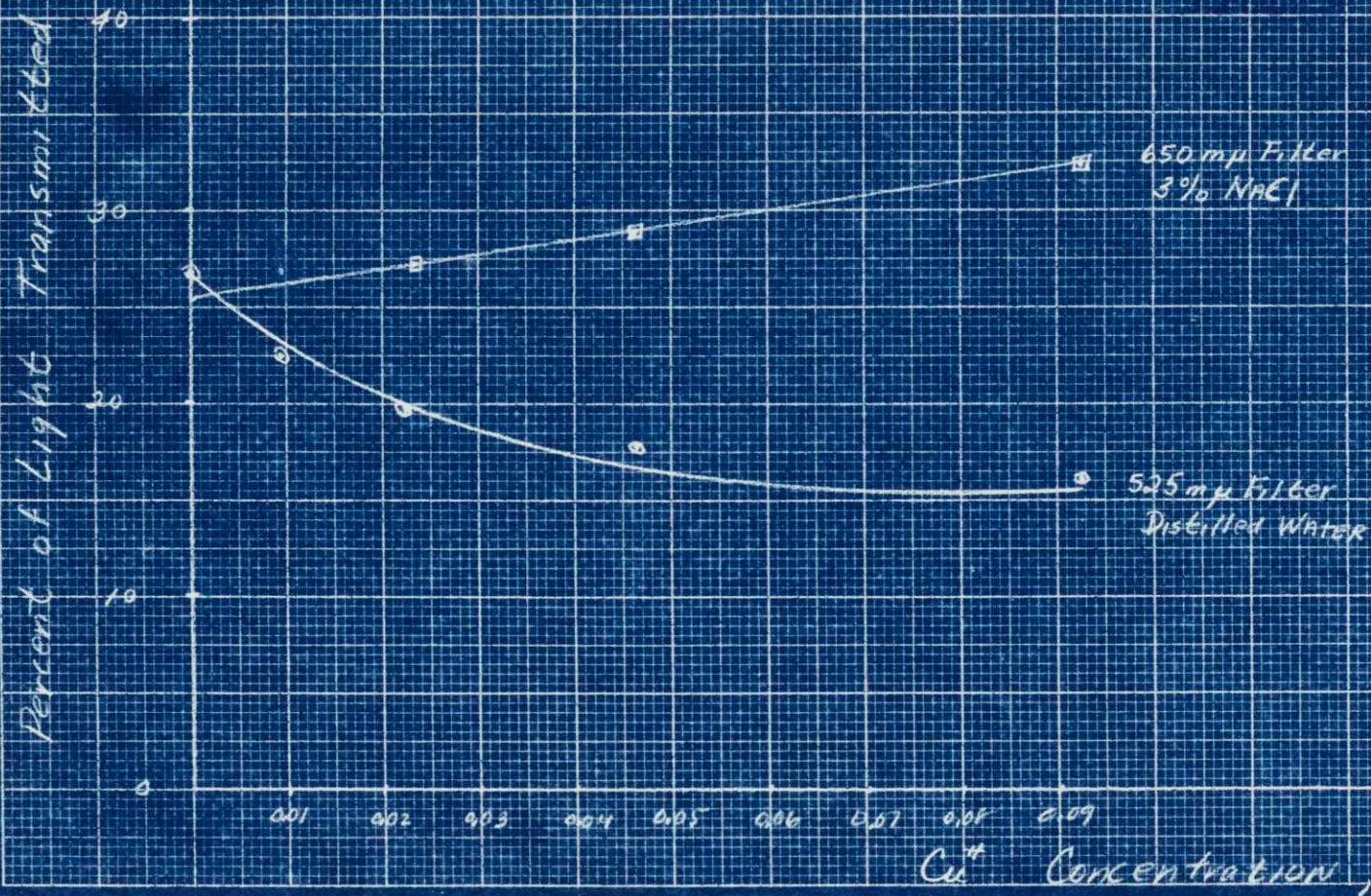
SUMMARY

Copper is subject to marked corrosive attack by aqueous solutions in turbulent flow. This thesis is concerned with the problem of determining the effect on corrosion of copper under varying conditions of O_2 concentration, velocity, pH and salt concentration of the corroding medium which is distilled water. Results are obtained for:

1.) the effect of varying velocities of flow of distilled water within the range 2 to 23 ft/sec.

2.) the effect of varying degrees of oxygenation of the water (amount of oxygen dissolved in the water) from 0.8 to 35 PPM.

3.) the effect of pH between 4.5 and 10.

4.) the effect of a 3% sodium chloride solution.

A copper tube is inserted in a closed system through which the distilled water is circulated by a stainless steel pump. The weight loss of the copper tube is determined after 24 hours. From this weight loss, the area exposed to corrosion, and the time of the run, the corrosion rate may be determined.

The results show:

1.) for solutions saturated respectively with air, pure oxygen, and pure nitrogen, the corrosion rate increases markedly with increased oxygen concentration i.e. is greatest for oxygen saturated water and smallest for nitrogen saturated water.

2.) the corrosion rate increases with increasing velocity in all runs.

3.) a 3% salt solution increases the corrosion rate 10 times that in ordinary distilled water.

4.) in the range pH 4 to 10, the corrosion rate decreases by a large factor and at pH 4.5 is 100 times that at pH 10.

These results indicate conclusively that the factors influencing the corrosion rate are those which determine the amount of oxygen brought to the metal-liquid interface. To minimize corrosion losses, the velocity of the solution in contact with the copper and the amount of dissolved oxygen should be held to the lowest value economically feasible. An acidic solution and dissolved salts should also be avoided if possible.

A study of corrosion over a wider range of pH and over a range of temperatures would be of interest.

INTRODUCTION

The field of metal corrosion study is a large one involving many variables. It involves such variables as temperature, surface roughness of the corroded metal, previous treatment of the metal, the nature and conditions of the corroding media and protective films which form on the metal. Corrosion studies are important industrially because plant and equipment shutdown, plus the cost and labor involved in replacing corroded material is costly. Corrosion rates must be determined empirically and under simulated working conditions for each metal.

This thesis investigates the effect of several variables upon the corrosion rate of copper. The corroding medium in all cases is distilled water, and with temperature and other factors constant, the variables examined are:

1.) velocity of distilled water in contact with copper.

2.) effect on corrosion of a 3% NaCl solution.

3.) effect of varying amounts of oxygen dissolved in water.

4.) pH of water.

A copper tube in which a hole had been previously drilled was placed in a closed system of circulating distilled water. Varying degrees of oxygenation were obtained by saturating the distilled water with either oxygen, air or nitrogen. pH of the solution of 8 and 10 was maintained with NaOH and pH of 4.5 was

maintained with CO_2. The velocity was varied by vary-
ing the mass flow rate of water through the sample.
Sodium chloride was used to obtain a 3% salt solution.
Making a number of runs of varying velocity and oxygena-
tion of both the distilled water and 3% salt solution
(pH kept approximately at 6), the weight loss of each
copper sample was determined. From this weight loss,
the area exposed to corrosion, and the time of the run,
the rate of corrosion in inches penetration per year
was calculated.

Graphical results are shown in a later section.
(Pgs. 13   ) Fish and Dankese (Course X thesis-1954)
found that the corrosion rate of copper increases with
increasing velocity and increasing oxygen concentration,
with which the results of this thesis are in agreement.

Theory of copper corrosion:

Comparision between iron and copper leads to an
understanding of the effect of several variables upon
copper corrosion. Iron corrodes in water by reacting
with H^+ as follows:

1.) $Fe + 2H^+ \longrightarrow Fe^{++} + 2H$

2.) $2H \longrightarrow H_2$
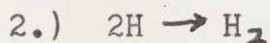
Therefore, the net reaction is:

3.) $Fe + 2H^+ \longrightarrow Fe^{++} + H_2$

Likewise, for copper, reation (1) is valid.

4.) $Cu + 2H^+ \longrightarrow Cu^{++} + 2H$ and

5.) $Cu + H^+ \longrightarrow Cu^+ + H$
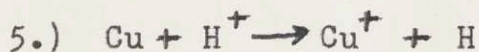
In copper corrosion both reactions (4) and (5) occur simultaneously. Since iron lies above hydrogen in the electromotive series, the driving force of the reaction to the right is large. Equilibrium would be obtained, thus inhibiting corrosion of iron, were it not for the fact that atomic hydrogen is formed in sufficient quantities to evolve as hydrogen gas; thus destroying the equilibrium and promoting corrosion. Copper, however, is below hydrogen in the electromotive series, and attains equilibrium at a concentration of atomic hydrogen insufficient to evolve hydrogen and thus promote corrosion. Therefore, the free energy of reaction is positive in absence of oxygen.

The rate of reactions (4) and (5) is increased (depolarized) by oxygen as follow, thus causing further corrosion.

6.) $2H + \frac{1}{2} O_2 \rightarrow H_2O$

Therefore, by adding reactions (4) and (6), one obtains:

7.) $Cu + 2H^+ + \frac{1}{2} O_2 \rightarrow H_2O + Cu^{++}$. This is the reaction by which copper corrodes in water.
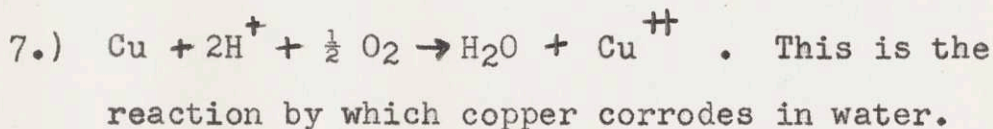
Likewise, by combining reactions (5) and (6), one obtains:

8.) $2 Cu + 2H^+ + \frac{1}{2} O_2 \rightarrow H_2O + 2 Cu^+$.
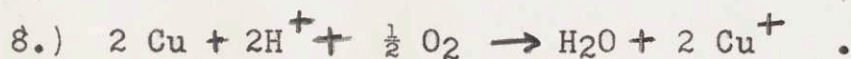
Reactions (7) and (8) are the corrosion equations for copper. Accompanying corrosion is the formation of a thin film of Cu_2O and $Cu(OH)_2$ on the metal surface which has a profound effect upon the corrosion rate.

The corrosion products, Cu_2O and $Cu(OH)_2$, tend to form a protective film on the surface of the copper, thus decreasing the rate of diffusion of oxygen to the surface. The above corrosion mechanism is further evinced by the fact that copper will not corrode appreciably in the absence of oxygen even in acid solutions.

Any factor which increases diffusion of oxygen to the metal surface will increase the rate of corrosion. The rate of diffusion may be increased by either increasing the oxygen concentration in solution, by decreasing the thickness of the stagnant layer of liquid through which the oxygen must diffuse or by dissolving the protective oxide film. Since the amount of oxygen in solution is, according to Henry's law, proportional to the partial pressure of oxygen above the solution, it may be controlled by bubbling various gases through the solution; i.e., either oxygen, air or nitrogen.

EFFECT OF VELOCITY

An increase in velocity has several effects upon corrosion. These are:

1.) Velocity reduces the thickness of the stagnant (laminar) layer of liquid next to the copper surface; hence, increasing the rate of diffusion of oxygen to the surface increases the corrosion rate.

2.) It hastens the removal of corrosion products and has an erosive effect upon any protective

films, such as Cu_2O or $Cu(OH)_2$. Both factors are favorable to a higher corrosion rate.

EFFECT OF pH

In general, protective films of copper oxide increase in stability with increasing pH.* Thus, the more basic the solution, the more effective the film is in preventing oxygen diffusion. Dissolved carbon dioxide is an acid, and can neutralize and dissolve the film, thus increasing corrosion rate.

EFFECT OF NaCl SOLUTION

The effect of a dissolved salt such as NaCl has been reported by several investigators with large discrepancies in the data. Qualitatively, it is accepted that NaCl will tend to produce soluble corrosion products and minimize the formation of Cu_2O and $Cu(OH)_2$. Also, chloride complexes are formed with liberated copper ions. ($CuCl_3^-$ and $CuCl_2^-$)

Sodium chloride, while possessing a large tendency to increase corrosion, may also decrease corrosion. A 3% salt solution slightly decreases the solubility of oxygen in solution and increases the viscosity of solution to a small extent. Both these factors have little influence in comparison with the increased corrosion effect of forming soluble corrosion products, thus neutralizing the oxide film.

* A major factor on the rate of corrosion is, in general, rate of formation of protective films.

Summarizing, all the above mechanisms mentioned affect either the total solubility of oxygen, or its rate of diffusion to the metal surface.

PROCEDURE

A section of 0.375 inch solid copper rod approximately five inches long constituted the sample. Samples of 0.125 to 0.297 inch inner diameter were used. The samples were drilled out with the help of kerosene, then reamed to the desired diameter. This procedure was followed in order to obtain a smooth inner surface. A Lucite insert was machined to fit each specimen and the dimensions were determined by a micrometer. The copper specimen was cleaned in benzene, desiccated for two hours and then set in the apparatus with the Lucite insert on the inlet end. The Lucite insert streamlines the flow and prevents impingement attack of the sample.

Previous to placing the specimen in the apparatus, it was weighted to the nearest tenth of a milligram. Three different concentrations of oxygen were examined by saturating the solution with either nitrogen, oxygen, or air. After saturating the solution with the desired gas for three hours, the pump was turned on. Both lines containing the copper specimens were clamped off at the beginning of the run, and the solution was pumped through a by-pass line in order to allow the system to reach a steady state. The pump itself and friction through the tubing brought the temperature of the solution to the operating conditions. This temperature was

was 32 $\pm 0.5°$C. for all runs.

During the run, distilled water was maintained at saturation by allowing the desired gas to pass into the water bottle from a gas tank and through a water trap. Thus, the solution was maintained at saturation by continual passage of the desired gas into the solution through the run. The rate at which the component is allowed to pass into the system was determined by maintaining a slightly positive gas tank pressure, as shown by a manometer located above the solution. The length of the experimental runs were all approximately 24 hours. At the end of a run the copper specimen was removed, placed in acetone to remove residual water, then cleaned and brushed in benzene. It was then desiccated for two hours and weighed to determine weight loss. From this weight loss and the area exposed to corrosion, the corrosion rate may be determined.

Two samples were run simultaneously, with an orifice placed in each line to determine the mass flow rate. From the mass flow rate and the cross-sectional area of each sample, the velocity was calculated. The orifices were calibrated by determining the mass rate of flow of water through each by weighing the quantity of water passed into a bucket for a measured time interval. A screw throttle on the Tygon tubing allowed the setting of the desired flow rates through each of the two samples.

A Winkler analysis for dissolved oxygen was made
by collecting the sample from a sampling valve which
was inserted into the line. One analysis for oxygen in
air, nitrogen and oxygen saturated distilled water and
salt solution was assumed to be a typical value for
saturation with that component. In the CO_2 saturated
run, air was simultaneously passed into the solution
with CO_2 to maintain saturation with both CO_2 and air.
For the nitrogen runs, when a Winkler analysis was
taken, the oxygen concentration in the solution was
too high (.94 PPM.), indicating a leak of air into the
system. It was found that a slight air leak through
the packing gland of the pump on the outlet side was
responsible for the high oxygen concentration. Three
different types of packing for the pump were used with
little success. However, Winkler analyses taken sev-
eral times during the run showed a variation of only
4% in the oxygen concentration. Since the leak was
small, and apparently constant, the value of the
oxygen concentration is reported with due regard to
the fact that there was a slight leak. This leak was
found to have little or no effect on oxygen concen-
tration during the oxygen and air saturated runs. The
volume of distilled water used was 37.8 liters in all
runs and a gas dispersion tube was used to increase
the rate of saturation of the solution. A color-
imetric copper analysis was made on the water at the
end of several runs to check the order of magnitude of

corroded copper. pH of solution was determined at the
start and end of each run with a Beckman pH meter.

The effect of 3% NaCl solution saturated with each
of the three gases: oxygen, nitrogen and air was
studied. Tests were also completed on air saturated
solutions of pH 4, 6, 8, 10 at a velocity of 10 ft./sec.
The solutions of pH 8 and 10 were maintained with NaOH,
and that of pH 4 was maintained by bubbling CO_2 through
the solution.

RESULTS

The results are presented in graphical form in figures 2 through 6 and tabulated in the appendix. Corrosion rate (R) is plotted versus velocity for both 3% NaCl and the distilled water solution. Three straight lines are obtained on each graph: one for each gas. A plot of corrosion rate versus pH at four different pH's (4.51, 6.6, 8.3, 10.1) is also presented. The corrosion rate is plotted versus oxygen concentration for five different velocities (0, 5, 10, 15, 20 ft./sec) for both the salt and distilled water solutions.

The results agree with those predicted by theory. Increasing velocity and oxygen concentration increases corrosion rate. As pH increases, the corrosion rate decreases by a large factor. The corrosion rate at a pH 4.5 is 53 times greater than that at pH 10. In the salt runs, the corrosion rate is about 100 times that in distilled water.

In the plots of corrosion rate versus velocity, straight lines are obtained. The slopes of these lines decrease with decreasing oxygen concentration.

For the graph of corrosion rate versus oxygen concentration for the five different velocities, the curves rise sharply, reach an inflection point then level off.

The plot of corrosion rate versus pH shows a decreasing negative slope with increased pH and a marked increase of corrosion rate with decreasing pH.

For the salt and distilled water runs, the pH of the distilled water from the tap varied from 6.31 to 6.71.

- Corrosion of Copper   T = 32°C

PLOT OF   AVERAGE
CORROSION RATE (R) -
INCHES PENETRATION
PER YEAR vs. VELOCITY

⊙ NITROGEN SATURATED
△ AIR SATURATED
☐ OXYGEN SATURATED
DISTILLED WATER

R

0.007
0.006
0.005
0.004
0.003
0.002
0.001

0   4   8   12   16   20   24

U, Velocity - ft./sec.
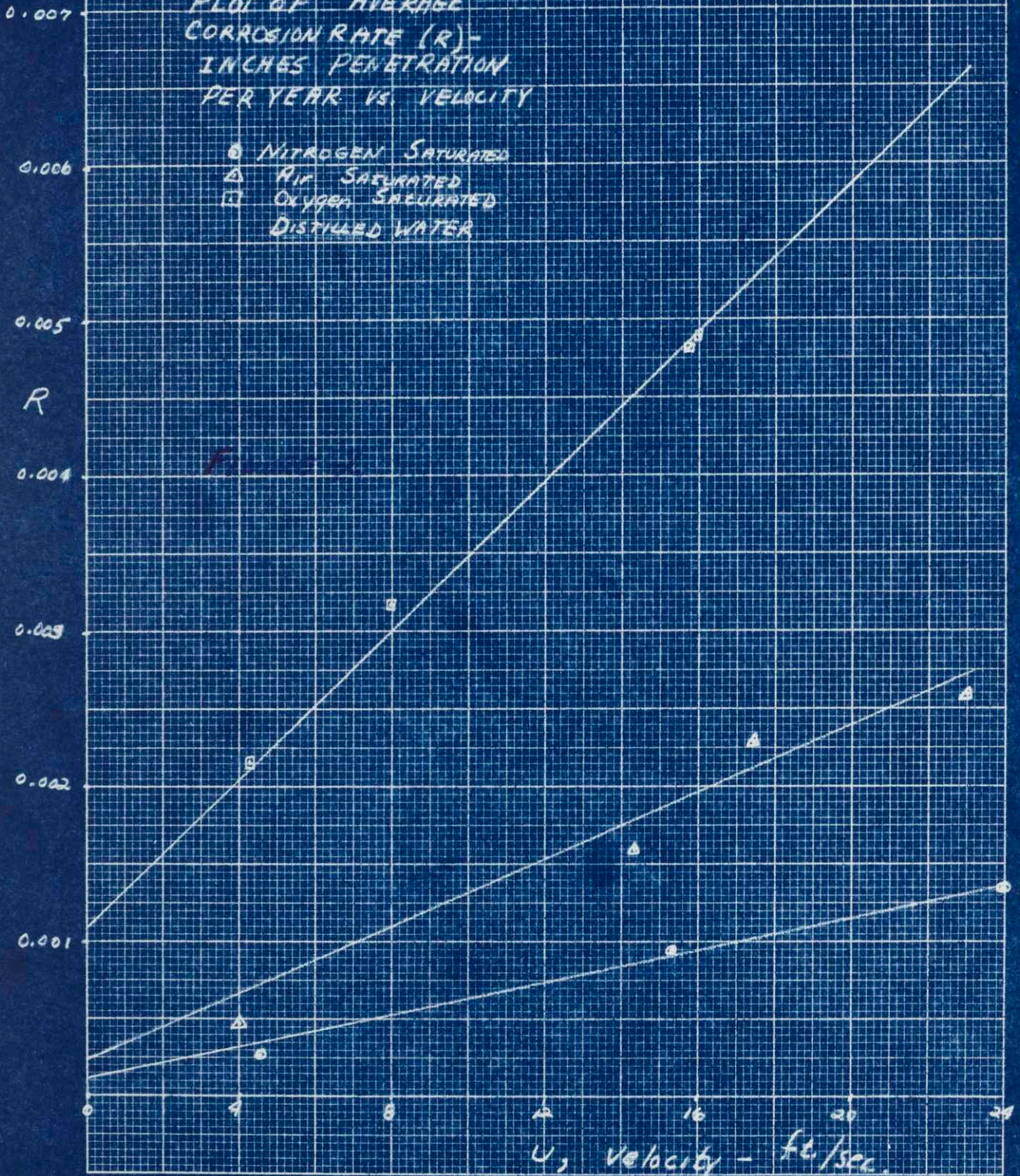
- Corrosion of Copper   T = 32°C -

Salt Solution

⊕ Nitrogen Saturated
△ Air Saturated
⊡ Oxygen Saturated

R - Average Corrosion Rate vs.
    Velocity, U -

R

U, Velocity - ft/sec
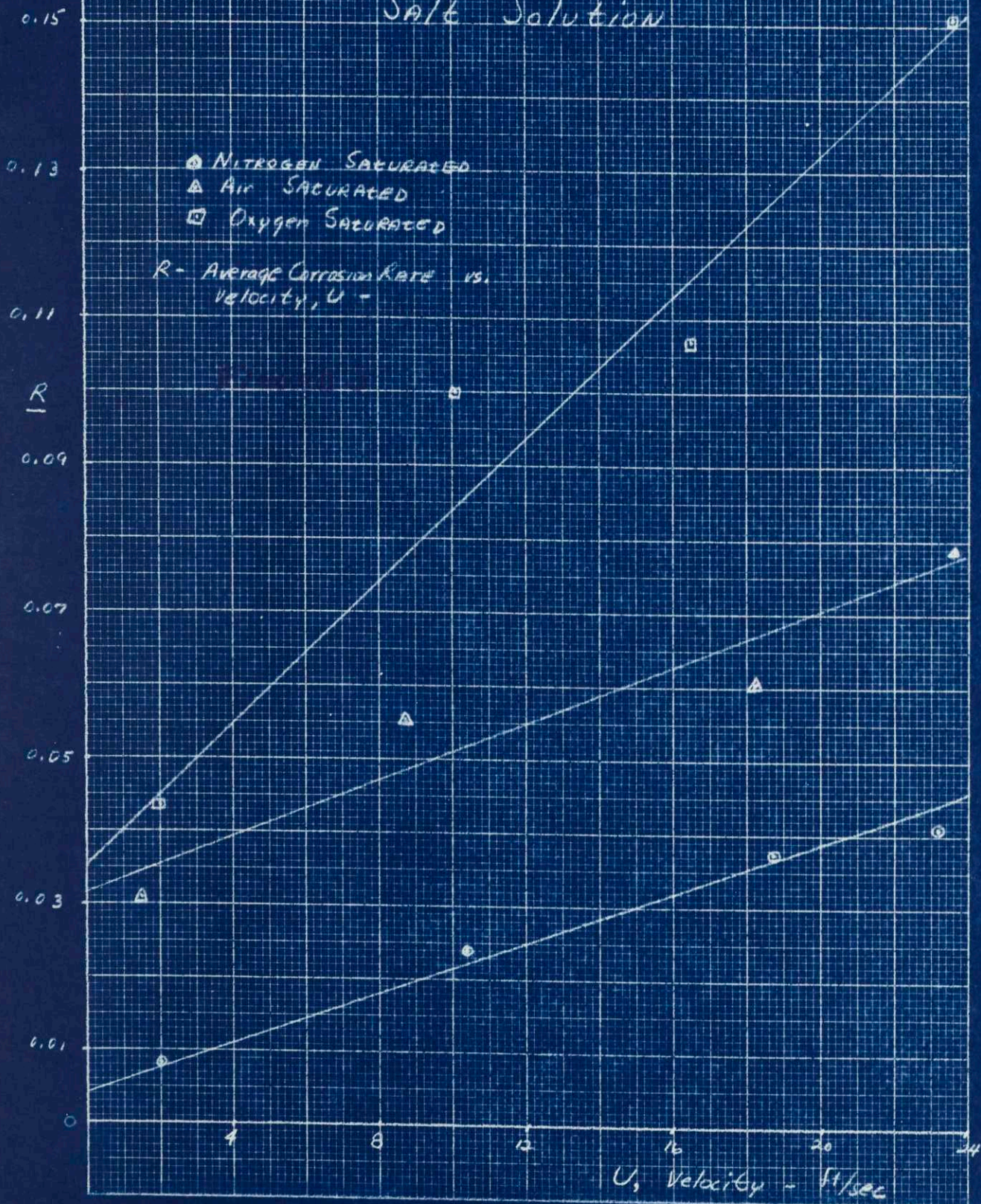
Corrosion of Copper
T = 32°C

Corrosion of Copper
T = 32 °F

Salt Solution

B, Average Corrosion Rate — Inches Penetration/Year

0.113
0.11
0.09
0.07
0.05
0.03
0.01

20 ft/sec
15 ft/sec
10 ft/sec
5 ft/sec
0 ft/sec

10   20   30
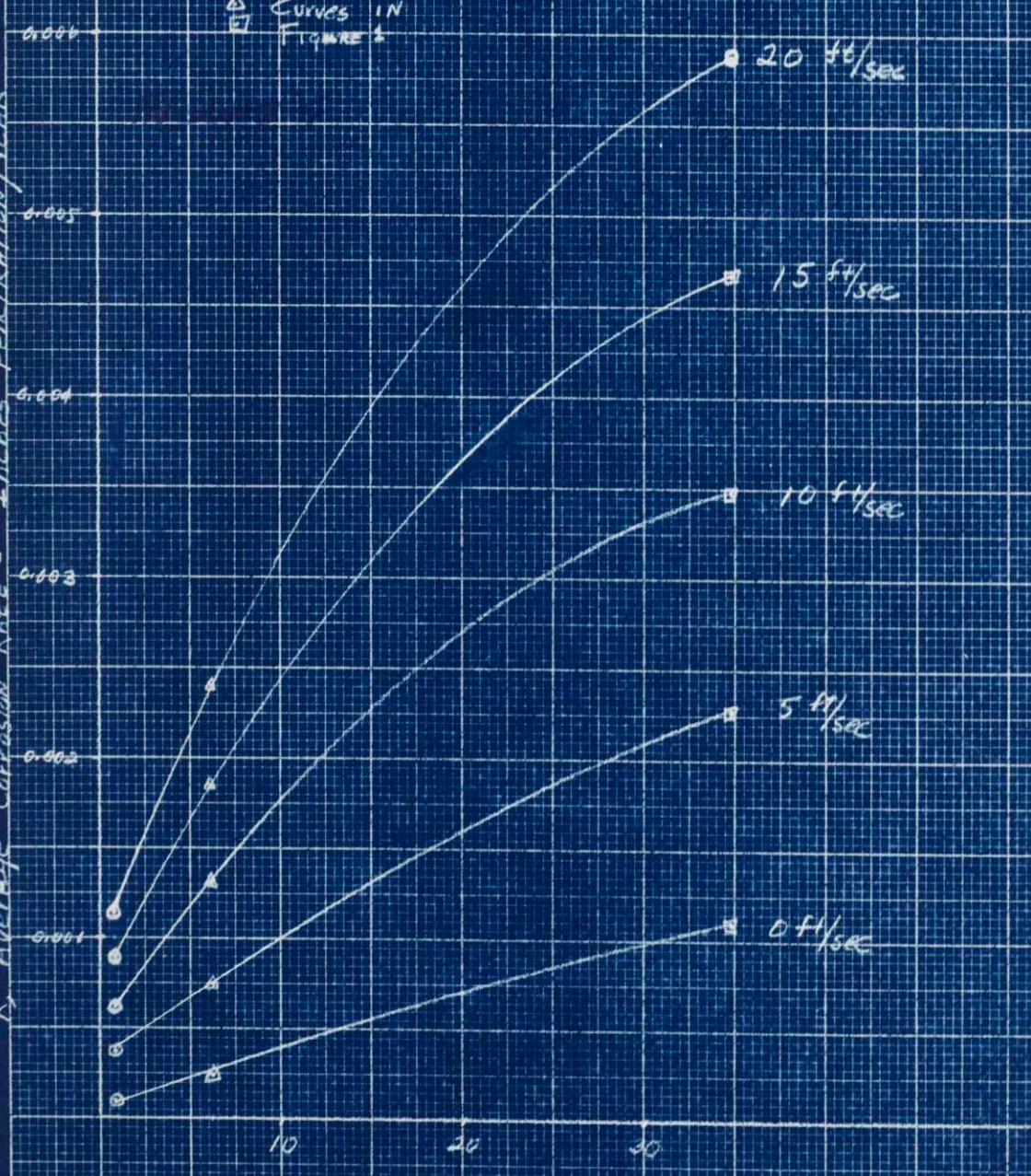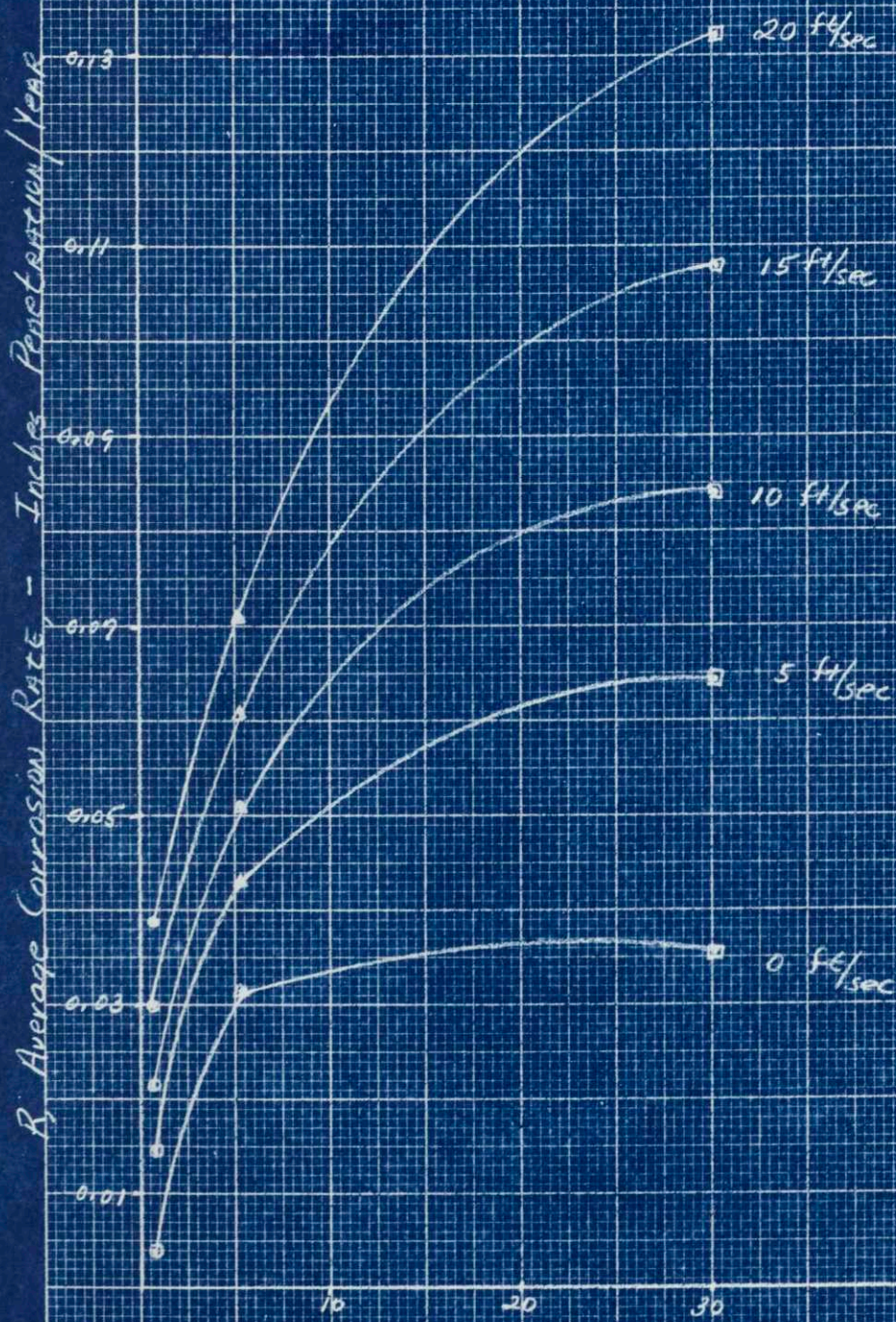
C, Dissolved Oxygen Concentration — P.P.M.
In Salt Solution (3%)

- Corrosion of Copper T=32°C -

PLOT OF AVERAGE
CORROSION RATE vs.
pH
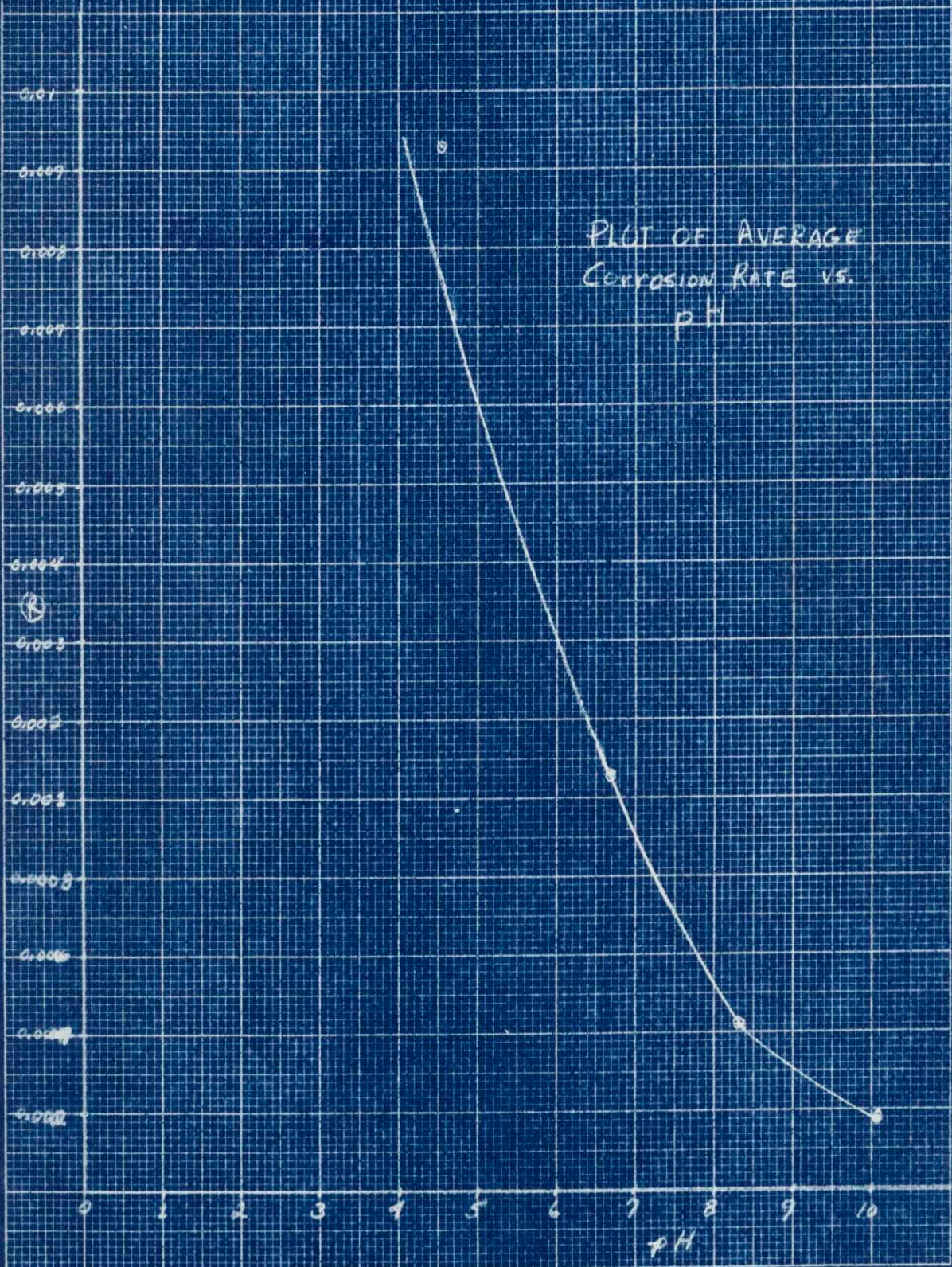
DISCUSSION OF RESULTS

As predicted by theory, the corrosion rate increases with increasing velocity, oxygen concentration and salt concentration and decreases with increasing pH. In all runs, the flow was turbulent as indicated by a calculation of Reynolds number for Run #8:

$$Re = \frac{D u \rho_w}{\mu_w}$$

$$Re = \frac{\frac{.1562}{12} \quad (2.04) \ (62.4)}{(0.84) \ (6.72 \times 10{-4})} = 2900$$

The transition from laminar to turbulent flow occurs at a Reynolds number of about 2100. Since this was the smallest Reynolds number, all runs were well in the turbulent flow region.

Since straight lines were obtained for the plots of corrosion rate versus velocity, the corrosion rate in both the distilled water and salt solutions is a linear or almost linear function of velocity.

Increased oxygen concentration has a marked effect on corrosion rate at low concentrations but approaches a limiting value and levels off. Thus, the limiting factors in corrosion at high oxygen concentrations are velocity, salt concentration and pH. This was true in both the salt and distilled water runs.

Zero velocity corrosion rates were obtained by extrapolation. The zero velocity corrosion rate of copper in 3% salt solution is .033 inch penetration per year. That reported for corrosion in salt water is 0. 002 per year. The discrepancy may be explained

by the fact that salt water is 2.6% salt, whereas the salt solution dealt with was 3%. Also, the pH of sea water is 8.1 to 8.3, whereas the pH's dealt with are in the range 6.3 to 6.7.

The lower pH and the higher salt concentration of this experiment tends to dissolve the protective film and increase the corrosion rate above that reported; also, the small amount of copper ions in solution may accelerate corrosion.

Comparision with Fish and Dankese show a comparative order of magnitude of corrosion rates. It must be remembered, however, that Fish and Dankese studied corrosion at a different temperature level and over a different range of pH values.

The large increase in corrosion rate in 3% salt solution indicates that the NaCl is extremely effective in forming soluble corrosion products and eliminating or minimizing the protective film. How effective the film is in protection of the metal is indicated by the fact that corrosion rate in 3% NaCl solution is approximately 100 times that in distilled water. Also, the corrosion rate at pH 4.5 is 53.4 times that at pH 10. The main effect then, of both low pH and dissolved NaCl is to dissolve the protective film; a factor which may affect corrosion rate by as much as a factor of 100.

As indicated by the plot of corrosion rate versus pH, the rate is not a linear function of pH.

CONCLUSIONS

1. The corrosion of copper by distilled water increases with oxygen concentration and velocity.

2. Increase of velocity results in increased corrosion rate and this effect becomes more pronounced as oxygen concentration is increased.

3. At low velocities, the average corrosion rate levels off with increased oxygen concentration. This occurs not only in the distilled water runs but also with the 3% salt solution runs.

4. As pH increases, the average corrosion rate decreases because of film stabilization.

5. The average rate of corrosion of copper is very high in 3% NaCl solution (pH $\simeq$ 6) because of the fact that there is probably a copper complex formed ($CuCl_3^-$ and $CuCl_2^-$).

Thus, the oxide film is made soluble by the formation of soluble chlorides and chloride complexes driving the corrosion reaction to the right; therefore, the corrosion rate is increased.

RECOMMENDATIONS

1. To reduce the corrosion of copper in any type of equipment, it is obviously an advantage to reduce the oxygen concentration and flow rate to the smallest possible amount.

2. A method for varying the oxygen concentration more completely should be attempted.

3. The same effects at different temperatures should be studied.

4. More extensive work should be done on the effect on corrosion by salt ~~salt~~ solutions and pH.

APPENDIX

PROCEDURE FOR THE DETERMINATION OF

DISSOLVED OXYGEN CONCENTRATION

The following analysis is found on pages 11 and
12, Ellis, M. M., Westfall, B. A. and Ellis, M. D.,
Determination of Water Quality, United States Govern-
ment Printing Office, Washington, 1946.

Reagents for the Winkler Analysis

1. Dissolve 700 gms. of pure KOH and 150 grams KI
in 750 ml. distilled water, and make up to one liter.

2. Place 480 gms. Mn SO_4-$4H_2O$ and 250 ml. distilled
water into a one liter volumetric flask. Continue the
addition of water until all the Mn SO_4 is dissolved.
Make up to one liter with distilled water. In place of
Mn SO_4. $4H_2O$, 400 grams of Mn SO_4-$2H_2O$ can be used.

3. The thiosulfate is standardized according to the
procedure found on pages 249-250 of Hamilton, L. F., and
Simpson, S. G., Quantitative Chemical Analysis, The
Hamilton Company, New York, (1955). The Standardization
was carried out with KB_rO_3. *

*It is recommended for standardization of thiosulfate,
that only high reagent purity KI be used. Most KI is
known to contain as an impurity, KIO_3 which liberates
I_2 and gives an erroneously low value for the normality
of the thiosulfate. This was the case in the first
standardization of thiosulfate, in which values obtained
for the oxygen concentration were in error by 40%. Re-
standardization gave new values of oxygen concentration
1.4 times that of those calculated previously.

PROCEDURE

1. A 250-300 ml. sample is desirable, and the sample bottle should be placed in a lead-lined box approximately 3 X 4 X 12 inches so that the corrosive chemicals and overflow will not foul other equipment.

2. Open sample bottle with great care, avoiding aeration of the surface of the sample with bubbles or by undue agitation, and add exactly one ml. of manganous sulfate solution from a glass pipette. The point of the pipette must be lowered an inch or more into the sample bottle and the heavy manganous sulfate solution introduced rather slowly so that it will sink to the bottom.

3. Add at once one ml. of alkaline-potassium-iodide reagent in a similar manner from another glass pipette.

4. Close bottle immediately and mix thoroughly by repeated rapid inversions of the bottle in the hand for 40 to 60 seconds. During this mixing, a milk-white precipitate of manganous hydroxide will form and as this compound combines with the dissolved oxygen in the water, yellowish-brown manganic compounds will appear. If the milk-white color persists, very little dissolved oxygen is present. After shaking the sample bottle for approximately one minute, return the bottle to the lead-lined box and allow the precipitate to settle at least halfway down the bottle, i.e., there should be no precipitate in the top half of the bottle when the next step is started.

5. Open sample bottle carefully as before and add two ml. of concentrated sulfuric acid (or hydrochloric acid) by bringing the point of the pipette against the neck of the sample so that the acid will flow down the inside wall of the bottle. Close bottle immediately after the acid is added and mix thoroughly by invert- ing the bottle several times. During this mixing, the precipitate, either white or brown, should dissolve completely and the sample will become clear, develop- ing a yellowish-brown color due to the iodine liberated. The depth of this color is proportional to the amount of dissolved oxygen present so that the analyst may estimate approximately the amount of dissolved oxygen present in the sample in advance of titration. Sometimes part of the precipitate will not dissolve owing to the formation of compounds other than the manganic compounds involved in the liberation of iodine, by the reaction of the reagents with the impurities in the water. If such an insoluble precipitate forms, it may be disregarded but care must be taken not to include any of the undis- solved precipitate in the aliquot portion of the sample taken subsequently for titration.

6. When the precipitate has dissolved and the sample has become uniformly colored, fill a 100-ml. graduated flask with the clear part of the sample (200-ml. may be used if greater accuracy in titration be desired). To the 100-ml. or 200-ml. aliquot taken from the first sample, add, from a pipette, the exact amount of treated sample lost by displacement when the manganous sulfate

and the alkaline-potassium-iodide solutions were
added during the process of fixation.   The volume
of this correction can be computed by substitution of
actual values in the following equation:

$$\frac{\text{ml. of treated sample taken}}{\text{ml. capacity of sample bottle}} \times \frac{\text{X ml. capacity of sample bottle}}{\text{ml. of manganous sulfate and alkaline potassium iodide}} = \begin{array}{l}\text{Total}\\\text{volume}\\\text{of treated}\\\text{sample}\\\text{required.}\end{array}$$

Pour the corrected aliquot sample into a 250-ml. beaker
and wash out the flask with a few ml. of distilled water,
adding the washings thus obtained to the sample in the
beaker.

7.   Titrate over a white surface with standardized
sodium thiosulfate solution until only a pale straw-
yellow color remains. Add 0.5 ml. (about 10 drops) of
starch solution and continue titration until the blue
color completely disappears for the first time. This
must be taken as the end-point as various impurities
in water may cause a return of the blue color a few
seconds to a few minutes after it is first discharged,
and if the titration is continued, an erroneously high
reading for the dissolved oxygen will be obtained....

COMPUTATION OF RESULTS

The sodium thiosulfate is standardized so that a
substitution of real values in the following equation
will give the dissolved oxygen in parts per million.

$$1000/A \times B \times F = X$$

where:

A equals ml. of aliquot (uncorrected, i.e., 100 or 200
   ml.) of treated sample.

B equals ml. if sodium thiosulfate is used in titration.

F equals factor value of one ml. of thiosulfate solution
   in milligrams dissolved oxygen.

X equals ppm. of dissolved oxygen in sample.

Limitations

Approximately one minute of mixing time must be
allowed after the addition of the manganous sulfate
and the alkaline-potassium-iodide solution so that the
consumption of the dissolved oxygen present in the water
by the manganous hydroxide formed from the reagents can
be completed. For uniformity, therefore, the mixing
should be timed rather accurately to be not less than
40 seconds nor more than 60 seconds. After the acid
is added, the titration should be made as soon as pos-
sible, for the sample is not dependable without special
treatment for more than one hour in this phase even if
very small quantities of ferric ion or various organic
substances are present. Although several procedures
for "fixing" the sample after the iodine has been
liberated have been proposed, they should be avoided
if possible as this procedure not only adds an additional
step to the routine, but may introduce errors of various
sorts.

SAMPLE CALCULATION FOR WINKLER ANALYSIS

Main Reaction: $4H^+ + O_2 + 4S_2O_3^= \rightarrow 2S_4O_6^= + 2H_2O$
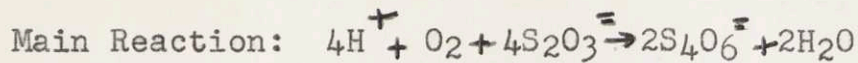
Milliequivalent weights oxidizing agent = milli-equivalent weights reducing agent.

$mewO_2 = mewS_2O_3^= = $ Normality $S_2O_3^=$ $x mlS_2O_3^=$

$= 0.1057$ x (4.12)

$= 0.435$

1 g mew $= 8.000$ mg of O_2

Therefore, mg. dissolved oxygen in 100 ml. of H_2O is equal to (0.435) x $8 = 3.48$ mg.

O_2 concentration $= 34.8$ ppm.

Oxygen Concentration in solutions:

O_2 Saturated Distilled Water $= 34.8$ ppm.

Air Saturated Distilled Water $= 6.28$ ppm.

N_2 Saturated Distilled Water $= 0.94$ ppm.

In 3% Salt Solution:

O_2 Saturated Salt Solution $= 30.1$ ppm.

Air Saturated Salt Solution $= 5.45$ ppm.

N_2 Saturated Salt Solution $= 0.81$ ppm.

DETAILS OF PROCEDURE

1. Air was passed through Ascarite to remove the carbon dioxide for the air runs.

2. Manometer readings were taken at several intervals throughout the runs and an average value was taken.

3. The Lucite inserts were machined from $\frac{1}{2}$ inch Lucite rods to streamline the flow and prevent impingement attack at the inlet end of the copper specimen.

4. The orifices were made by drawing out two short pieces of $\frac{1}{2}$ inch glass tubing so that the orifices were approximately $\frac{1}{4}$ inch in diameter.

5. The throttles which regulated the mass flow rate through each sample were placed 24 inches from the upstream end in order to allow the water to attain steady flow conditions.

6. Two jugs were used and saturated simultaneously in order to minimize the time interval between runs.

PROCEDURE FOR THE DETERMINATION OF COPPER IN WATER

The following analysis is found on pages 220 and
221, E. G. Sandell, Colorimetric Determination of
Traces of Metals, Interscience Publishers, Inc., New
York, New York, 1944.

1. Dithizone - 0.001 - 0.0012 per cent $\frac{\text{weight}}{\text{volume}}$

    is dissolved in carbon tetrachloride. The latter
    must be of reagent quality. The water used should
    be distilled and copper-free. The hydrochloric
    acid should also be nearly copper-free.

2. Next, the standard copper solution should be pre-
    pared by dissolving 0.1964 grams of clear unef-
    floresced crystals of $CuSO_4.5H_2O$ in water, and
    adding enough hydrochloric acid to make the final
    acidity about O.I N and dilute to 500 ml. From
    this solution, a weaker one can be made by dilu-
    tion with O.I N hydrochloric acid.

3. The photolometer is first calibrated using sol-
    utions of known copper concentrations.

4. The sample solution, of 10 ml. should contain not
    more than 5 γ of copper if 5 ml. of dithizone are
    to be used. Make ths solution 0.05-0.I N in
    hydrochloric acid and shake for two minutes in a
    small seporitory funnel with 5.0 ml. of 0.001
    percent dithizone (delivered from a pipette). The
    color of the final solution should deviate from
    that of a pure copper dithizonate solution.

5. Allow a few drops of carbon tetrachloride flow out of the funnel to displace any aqueous solution in the bore of the stopcock and dry the stem of the funnel with filter paper. Deliver the carbon tetrachloride into a suitable cell and cover the latter to prevent evaporation. The solution should be entirely clear.

SAMPLE CALCULATIONS OF CUPRIC ION DETERMINATION USING
FISHER PHOTOELECTROMETER

Samples of known cupric ion concentration in ppm. were placed in the photoelectrometer using a 650 mμ and a 525 mμ filter, and the percentage of light transmitted was recorded for each. These values are represented by the calibration curve, Figure 8.

Since the copper weight loss and the volume of water used were known, the theoretical copper concentration could be determined and compared with the values found by the above method.

RUN	FILTER USED	COMBINED WT. LOSS GMS.	VOLUME GMS. H_2O	THEORETICAL PPM.	PHOTO VALUE PPM.
6	525	0.0050	37800	0.154	0.051
8	650	0.1703	37800	4.5	0.325
9	650	0.2606	37800	6.88	0.464
10	650	0.3446	37800	9.10	0.232
11	650	0.0582	37800	1.54	0.33
12	650	0.0433	37800	1.15	0.31

The comparison between the theoretical concentration and that obtained from the photoelectrometer indicates a correct order of magnitude. Discrepancies occur because inaccuracy of the machine at such low values and from washing corrosion products off in benzene after the run.

In the salt runs (8 to 12), the theoretical value of copper concentration ranges from 3.7 to 35.2 times as great as that obtained from the meter.

In run (6), the theoretical value is only 3 times
as great as that obtained by the meter. The large
difference between the theoretical and meter value
ppm. in the salt runs indicates that much of the
copper in solution is in the form of complexes
($CuCl_2^-$ and $CuCl_3^-$). Thus, the hypothesis that
NaCl will form soluble chloride complexes and
increase corrosion rate by destroying the oxide
film is a valid one.

Comparison of the value of the experimental
copper concentration in Run 6 with the value ob-
tained by the meter method can be used as indica-
tion of the effect of velocity in washing away the
corrosion products. For instance, the meter value
for Run 6 gives a value 1/3 that predicted by the
weight loss. Therefore, only 1/3 of the corrosion
products formed in Run 6 have been washed from the
copper surface.

DETAILS OF CALIBRATION OF ORIFICES

The system was arranged as shown in Figure 1 except that the Tygon tubing could be transferred from the twenty gallon bottle to a calibrated bucket easily. The orifices were glass tubing constricted down, with glass T's at the ends which were connected to the manometer. The water was allowed to flow through these orifices and they were calibrated. All air bubbles were bled from all leads and the manometer. The flow rate was then adjusted by means of a throttle clamp on the Tygon tubing. The amount of water pumped through the system in a measured time interval was then recorded. The same procedure was repeated for ΔP's varying from a maximum at no throttling to a minimum at zero flow rate. These results are plotted for both orifices on Figure 7. For a centrifugal pump, $m = u A_i \rho =$ constant.

SAMPLE CALCULATIONS

1. Calculation of the Corrosion Rate (Run 6): $R = \dfrac{WK}{SAT}$ (1)

     S - Density of copper 8.92 $\pm$ 0.01 g/cm^3

     W - Weight before, minus weight after run- 0.0054$\pm$0.0001 g

     K - Constant of proportionality - 0.06102 $\dfrac{in^3}{cm^3}$

     T - Time in years - 0.0028 $\pm$ 0.00001 yrs.

     A -   (3.14) (0.1502) (5.906)- 4.48 $\pm$ 0.01 in^2

Therefore: R - (0.0054) (0.06102) / (8.92) (4.48)(0.0028)

$$R = 0.00491 \text{ in / yr.}$$

Error Analysis:

$$R = \frac{WK}{SAT}$$

$$\Delta R = \left| \left(\frac{\partial R}{\partial W}\right) \Delta W \right| + \left| \left(\frac{\partial R}{\partial A}\right) \Delta A \right| + \left| \left(\frac{\partial R}{\partial T}\right) \Delta T \right|$$

$$\frac{\partial R}{\partial W} = \frac{K}{A \times T} \qquad \frac{\partial R}{\partial A} = -\frac{WK}{A^2 T} \qquad \frac{\partial R}{\partial T} = -\frac{WK}{AT^2}$$

$$\Delta R = \left| \left(\frac{K}{AT}\right) \Delta W \right| + \left| \frac{WK}{A^2 T} \Delta A \right| + \left| \frac{WK}{AT^2} \Delta T \right|$$

$$\Delta R = \frac{WK}{AT} \left(\frac{\Delta W}{W} + \frac{\Delta A}{A} + \frac{\Delta T}{T} \right)$$

% Error

$$\% \text{ ERROR} = \frac{\Delta W}{W} + \frac{\Delta A}{A} + \frac{\Delta T}{T}$$

$$= \frac{0.0001}{0.0054} + \frac{0.01}{4.48} + \frac{0.00001}{0.0028}$$

$$= 2.44 \%$$

The percentage error in R varies from:

In Distilled Water Runs:

   20.9% to 4.03% for the Air runs

   40.2% to 7.9% for the N_2 runs

    4.8% to 2.2% for the O_2 runs

In Salt Runs:

   0.37% to 0.01% for the Air runs

   1.47% to 0.17% for the N_2 runs

   0.23% to 0.045% for the O_2 runs

2. Calculation of Velocity (Run 1):   (3)

$$u \,(\text{ft/sec}) = \frac{m \,(\text{lb./sec})}{A_i \,(\text{ft.}^2) \times \rho_w \left(\frac{\text{lb.m.}}{\text{ft}^3}\right)}$$

To find m, the mass rate of flow, use the calibration

curve:

$$\Delta P = 0.5 \pm 0.01 \text{ inches}$$
$$m = 14.3 \text{ lbm/sec}$$
$$\rho_w = 62.4 \text{ lbm/ft}^3$$

To find the cross-sectional area of the sample:

   D = 0.1285 0.0001 inches

$$A_i = \frac{\pi D^2}{4} = 0.785 \frac{(0.1285)^2}{12}$$

Therefore:

$$u = \frac{14.3}{(A)\,(62.4)} = 14.3 \text{ ft/sec}$$

The percentage error is approximately equal to 1.1%.

SUMMARY OF DATA AND CALCULATED VALUES

RUN NO.	1	1	2	2	3	3
LINE NO.	1	2	1	2	1	2
DIAMETER OF SPECIMEN HOLE (IN.)	.1607	0.1285	0.2812	0.2515	0.1285	0.250
LENGTH OF EXPOSED SPECIMEN (IN.)	6.00 / 6.00	5.908	5.015	5.015	6.00	5.187
TOTAL AREA EXPOSED (IN.^{2} $(A = \pi DL)$	3.05	2.308	4.43	3.96	2.42	4.06
VELOCITY (FT./SEC.)	3.98	14.3	17.3	23	4.5	15.3
TEMP. °C	32°C	32°C	32°C	32°C	32°C	32°C
pH	6.41	6.41	6.44	6.44	6.35	6.35
GAS COMPONENT	AIR	AIR	AIR	AIR	N2	N2
OXYGEN CONC. IN PPM.	5.71	5.71	5.71	5.71	.94	.94
SOLUTION	Dist. Water	Dist. Water	Dist. Water	Dist. Water	Dist. Water	Dist. Water
LENGTH OF RUN (YRS.)	0.00275	.002625	.0031	.0026	0.0031	0.0021
WT. LOSS (GRAMS)	1.0006	.0014	.0046	.0039	0.0013	0.0029
CORROSION (IN. PENETRATION PER YEAR)	.000494	0.0016	0.0023	0.0026	0.00027	0.00095

RUN NO.	4	5	5	6	6
LINE NO.	1	1	2	1	2
DIAMETER OF SPECIMEN HOLE (IN.)	0.250	0.125	0.282	0.152	0.284
LENGTH OF EXPOSED SPECIMEN (IN.)	5.341	6.01	5.641	5.906	5.015
TOTAL AREA EXPOSED (IN.^{2} ($A = \pi DL$)	4.06	2.36	4.56	2.82	4.48
VELOCITY (FT./SEC.)	24	4.15	8.0	15.9	16.0
TEMP. $^\circ$C	32°	32°	32°	32°	32°
pH	6.7	6.31	6.31	6.41	6.41
GAS COMPONENT	N_2	O_2	O_2	O_2	O_2
OXYGEN CONC. (IN PPM.)	.94	34.8	34.8	34.8	34.8
SOLUTION	Dist. Water	Dist. Water	Dist. Water	Dist. Water	Dist. Water
LENGTH OF RUN (YRS.)	.0026	0.0029	0.0029	0.00289	0.00289
WT. LOSS (GRAMS)	.0039	0.0022	0.0040	0.0059	0.0093
CORROSION (IN. PENETRATION PER YEAR)	0.00135	0.00215	0.0318	.00488	.00491

RUN NO.	7	7	8	8	9	9
LINE NO.	1	2	1	2	1	2
DIAMETER OF SPECIMEN HOLE (IN.)	1.285	0.2812	0.1562	0.286	0.1562	0.297
LENGTH OF EXPOSED SPECIMEN (IN.)	5.845	5.015	5.923	5.031	5.892	5.015
TOTAL AREA EXPOSED (IN.^{2} $(A = \pi D L)$	2.362	4.43	2.90	4.52	2.88	4.67
VELOCITY (FT./SEC.)	1.425	23.6	8.67	18.2	2.04	10.4
TEMP °C	32°	32°	32°	32°	32°	32°
pH	6.64	6.64	6.61	6.61	6.69	6.69
GAS COMPONENT	AIR	AIR	AIR	AIR	AIR	AIR
OXYGEN CONC. (IN PPM.)	5.45	5.45	5.45	5.45	.81	.81
SOLUTION	3% salt solution	3% salt solution	3% salt solution	3% salt solution	3% salt solution	3% salt solution
LENGTH OF RUN (YRS.)	0.0027	0.0027	0.0026	0.0026	.0020	.0020
WT. LOSS (GRAMS)	0.0242	0.1264	0.0651	.1052	.0068	.0514
CORROSION (IN. PENETRATION PER YEAR)	.0310	.0789	0.0585	.0609	.00809	.024

RUN NO.	10	10	11	11	12	12
LINE NO.	1	2	1	2	1	2
DIAMETER OF SPECIMEN HOLE (IN.)	0.152	0.284	.1562	.1607	.286	.2515
LENGTH OF EXPOSED SPECIMEN (IN.)	5.906	5.015	6.00	5.904	5.156	5.172
TOTAL AREA EXPOSED (IN^2) $(A = \pi D L)$	2.82	4.48	2.95	2.98	4.63	4.08
VELOCITY (FT./SEC.)	18.65	23.2	2.04	10.91	16.5	23.6
TEMP. $^{\circ}$C	32°	32°	32°	32°	32°	32°
pH	6.71	6.71	6.55	6.55	6.70	6.70
GAS COMPONENT	N_2	O_2	O_2	O_2	O_2	O_2
OXYGEN CONC. (IN PPM.)	.81	30.1	30.1	30.1	30.1	30.1
SOLUTION	3% salt solution	3% salt solution	3% salt solution	3% salt solution	3% salt solution	3% salt solution
LENGTH OF RUN (YRS.)	0.0029	0.0029	.0024	.0029	.0029	.0024
WT. LOSS (GRAMS)	0.0452	0.0643	.0448	.1291	.2155	.2158
CORROSION (IN. PENETRATION PER YEAR)	.0377	.0410	30.2	.0437	.1000	.1510

RUN NO.	13	14	15	16
LINE NO.	1	1	1	1
DIAMETER OF SPECIMEN HOLE (IN.)	0.125	0.2812	0.1607	0.1645
LENGTH OF EXPOSED SPECIMEN (IN.)	6.01	5.172	5.820	5.890
TOTAL AREA EXPOSED (IN.^{2} $(A = \pi DL)$	3.05	4.56	2.95	3.04
VELOCITY (FT./SEC.)	10	10	10	10
TEMP. $^{\circ}$C	32°C	32°C	32°C	32°C
pH	6.6	8.3	10.1	4.51
GAS COMPONENT	AIR	AIR	AIR	AIR
OXYGEN CONC. (IN PPM.)	5.71	5.71	5.71	5.71
SOLUTION	Dist. water	Dist. water	Dist. water	Dist. water
LENGTH OF RUN (YRS.)	0.00275	0.0030	0.0026	0.0026
WT. LOSS (GRAMS)	.0029	.0015	0.0004	0.0107
CORROSION (IN. PENETRATION PER YEAR)	0.0013	0.000748	0.000352	.00938

NOMENCLATURE

A   Exposed area of specimen (ln.^{2})

Ai   Cross-sectional area of copper tube (ft.^{2}).

C   Concentration of dissolved oxygen (ppm.).

D   Diameter of copper specimen (inches).

K   Constant of proportionality (in^3/cm^3).

M   Mass rate of flow (lbs/sec).

mew   Milliequivalent weight.

ΔP   Difference in levels of manometer fluid.

PPM.   Concentration in parts / million parts water.

R   Corrosion rate (inches penetration/year).

Re   Reynolds number.

T   Duration of run (years).

u   Linear velocity through specimen (ft/sec).

W   Weight loss of specimen (grams).

L   Length of copper tube exposed to water (inches).

μ_w Viscosity of water lbm/sec x ft.

ρ_w Density of water, lbm/ft.^{3}.

S Density of copper, grams/cm^3.

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