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Chemical studies of the liquid within a growing stress corrosion crack in brass

Roy H. Kissinger
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CHEMICAL STUDIES OF THE LIQUID WITHIN A
GROWING STRESS CORROSION CRACK IN BRASS

by

Roy H. Kissinger

A Research Report

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Chemical Engineering

Lehigh University

April, 1971

This research report is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Henry Reichert, Jr.
Professor in Charge

July 23, 1971
Date

Leonard A. Wilson
Chairman of Department

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ABSTRACT

Studies are reported on the chemistry within a stress corrosion crack in 70:30 brass (CDA Alloy #260) propagating in 15N ammonium hydroxide containing 8 grams/liter dissolved copper. The liquid in the crack was isolated for study by removing the specimen from solution, immersing the specimen in liquid nitrogen to freeze the liquid within the crack, fracturing the sample, and removing the liquid once it had thawed.

Spectrophotometric analysis of the liquid indicated a copper concentration of 14.5 grams/liter and a zinc concentration of 11.5 grams/liter after $1\frac{1}{4}$ to $1\frac{1}{2}$ hours of immersion. The relative dissolution rates of copper and zinc were thus in a 35:65 ratio as compared to the 70:30 ratio of these elements in the alloy. Severe dezincification occurred within the crack. The total corrosion rate in the crack was estimated to be between 3×10^{-6} and 7×10^{-6} grams/square/centimeter minute. Specimens of the same brass immersed in the ammonium hydroxide-copper ion solution under similar experimental conditions yielded weight loss corrosion rates of 5.4×10^{-6} grams/square centimeter/minute. The corrosion rate within the crack was thus approximately the same as the corrosion rate of the specimen as a whole.

pH measurements of the liquid within the crack indicated no measurable difference from that of the bulk solution.

The Pourbaix diagrams were calculated for pure copper and pure zinc immersed in 15N ammonium hydroxide containing 8 grams/liter dissolved copper. Potential and pH measurements made on stressed brass specimens indicated that the zinc should dissolve with the formation of $\text{Zn}(\text{NH}_3)_4^{2+}$ and that the copper forms a four-phase equilibrium between cuprous oxide, cupric oxide, $\text{Cu}(\text{NH}_3)_2^+$ and $\text{Cu}(\text{NH}_3)_4^{2+}$.

Conductivity measurements on 15N ammonium hydroxide solutions indicated that dissolved copper and zinc appreciably increase the solution conductivity.

The tendency of 70:30 brass to undergo stress corrosion cracking in concentrated ammonium hydroxide solution containing dissolved copper is a result of dezincification at the base of the crack and consequent weakening of the matrix. The high conductivity of the solution within the crack presumably enhances local cell action within the crack.

I. INTRODUCTION

Corrosion can be of two basic types: (1) uniform corrosion or (2) localized corrosion. The phenomenon of stress corrosion cracking or season cracking, as it was first known, is a form of localized corrosion.

Stress corrosion cracking is a macroscopically brittle fracture of metals and alloys in specific chemical environments at residual or applied tensile stresses below those which would cause fracture in the absence of the environment^{1,2}. Therefore, stress corrosion cracking is the result of combined stress and corrosion.

Although stress corrosion cracking occurs in nearly all types of metals and alloys³, it first came into prominence in the early part of this century when brass cartridge cases being used by the British Army in India developed, at first unexplainable, cracks⁴. An investigation determined that the cracks were stress corrosion cracks resulting from internal stresses of the cases and the ammonia in the stables where the cartridges had been stored.

Since that time, stress corrosion cracking of brass has been observed in the costly failure of industrial piping, air conditioning condenser coils, and many other applications where the conditions necessary for stress corrosion cracking were present.

The conditions necessary for stress corrosion cracking can be expressed symbolically in terms of the probabilities

that the various controlling factors are present. This expression for the probability of stress corrosion cracking in brass is given by Thompson³, as follows:

$$P_c = P_{NH_3} \cdot P_{H_2O} \cdot P_{AIR} \cdot P_S \cdot P_{ALLOY}$$

where P_c is the probability that stress corrosion cracking will occur.

P_{NH_3} is the probability that a concentration of ammonia sufficient to cause cracking is present.

P_{H_2O} is the probability that a concentration of water sufficient to cause cracking is present.

P_{AIR} is the probability that a concentration of air sufficient to cause cracking is present.

P_S is the probability that a stress load sufficient to cause cracking is present.

P_{ALLOY} is the probability that the alloy present is susceptible to stress corrosion cracking.

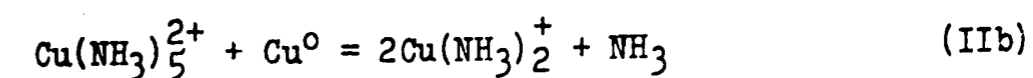
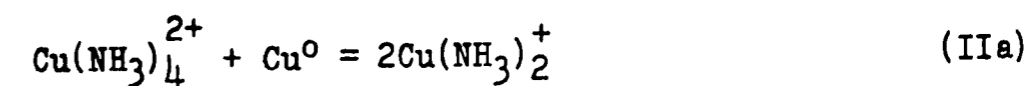
Since the probability of stress corrosion cracking in brass has been related to the five parameters above, it is obvious that a thorough understanding of the interaction of these parameters must be had if the costly phenomenon of stress corrosion cracking in brass is to be understood and controlled.

Therefore, this study was undertaken to investigate through analytical analysis and other physical chemical tests the entrained liquid in a growing stress corrosion crack of brass. It is hoped that the results of this study, when viewed with the work of previous researchers, may help in establishing a better understanding of the phenomenon of stress corrosion cracking of brass.

II. THEORETICAL BACKGROUND

Two general classes of models for stress corrosion cracking in brass have been suggested: (1) the dissolution model and (2) the mechanical model.

The dissolution model considers that failure occurs by a dissolution-dependent process involving the reduction of the aqueous cupric complexes by reactions of the type given in IIa and IIb⁵.

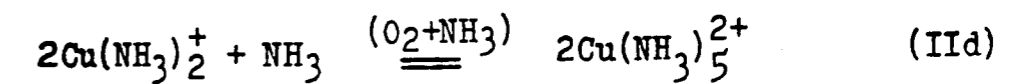
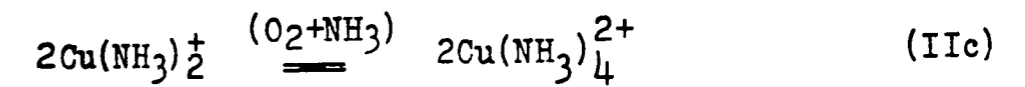


This analysis of a stress corrosion mechanism was first suggested by Mattsson⁶ from comparison of his stress corrosion data in the range of pH 3.9-4.7 with the Pourbaix diagrams for copper and zinc. The potential-pH diagrams suggested the reduction of Cu^{2+} to either Cu^+ or Cu_2O to be a cathodic process with the selective dissolution of zinc as the anodic process.

Although ammonia is not involved in the net reaction of Cu^{2+} to either Cu^+ or Cu_2O , Mattsson suggested that the ammonia increases the rate of the reaction by acting as a complexing agent to maintain the Cu^+ in solution as shown by reaction of the type given in IIa.

In the pH range 3.9-4.7, no tarnish film is formed and Mattsson's suggestion of increased reaction rate with increased cupric complex concentration has been supported by

Pugh et al.⁷, who showed that the time to failure decreased with increased complex ion concentration. They suggested that the effect of complex ion concentration could be explained by the autocatalytic reactions of the type given in IIc and IIId, which result not only in regeneration of the cupric complex ions reduced in reactions of the type given in IIa and IIb, but also in formation of new cupric complex ions.



These newly formed cupric complex ions would increase the cupric complex ion concentration and could be expected to increase the cathodic half reaction in the overall electrochemical corrosion.

The proposed autocatalytic model requires oxygen for the regeneration of the cupric complex ions, therefore a lack of oxygen should prevent stress corrosion cracking by this model.

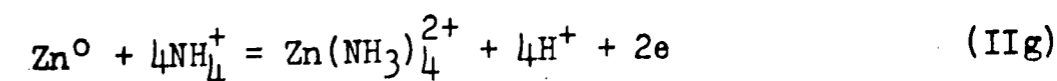
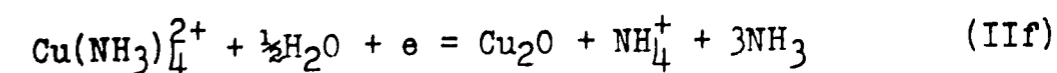
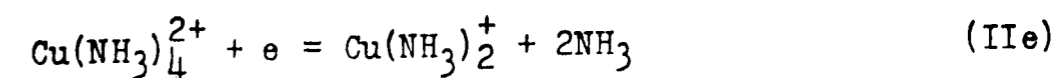
Johnson and Leja⁸ have demonstrated this behavior by sealing a stressed brass specimen and a solution of cupric-amine complex in a test tube. The solution became colorless in a few hours and no cracking was observed for periods of 30-40 days. However, within minutes of opening the test tube to the air the color returned and within several hours the specimen had cracked.

Since none of the foregoing equations involve an alloying element and since Pugh et al.⁹ have shown that in non-

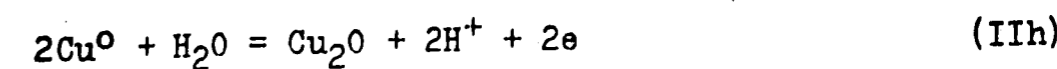
tarnishing solutions the time to failure is independent of the zinc content of the brass, one would expect to find stress corrosion cracking of pure copper in non-tarnishing solutions. Pugh et al.^{9,10} have found stress corrosion cracking of pure copper in solutions having a high concentration of the $\text{Cu}(\text{NH}_3)_5^{2+}$ complex ion.

The foregoing discussion has been limited to the chemical considerations of a continuous electrochemical dissolution model with non-tarnishing solutions, in which the stress corrosion crack is intergranular.

Hoar and Booker¹¹ have extended the dissolution model to tarnishing solutions, where stress corrosion cracking is transgranular. They postulated that the tarnish film is formed first by the cathodic reduction of aqueous copper (II) by reactions of the type given in IIe and II f, with the concomitant reaction being anodic zinc dissolution by a reaction of the type given in IIg.



When the brass matrix is reduced in zinc content, a rapid conversion of "activated" porous copper to cuprous oxide takes place by a reaction of the type given in IIh.



This postulation led to a mechanism of crack initiation arising from localized dezincification, with formation of cuprous oxide film intensifying local attack at grain boundaries and with subsequent rapid crack propagation involving a single-stage yield-assisted anodic dissolution of zinc at the crack tip. This concept implies that the same mechanism is operative in tarnishing and non-tarnishing solutions and that the tarnish layer prevents the dissolution within a grain, but that dissolution can occur at grain boundaries due to the porosity of the tarnish film, as suggested by Mattsson. These conclusions are consistent with the observations of intergranular cracking in non-tarnishing solutions and transgranular cracking in tarnishing solutions.

The extension into tarnishing solutions leads to the consideration of mechanical models, which advocate a very rapid mechanical fracture of a brittle film chemically formed at a slower rate.

This concept of a tarnish-rupture mechanism was first postulated by Forty and Humble¹², who demonstrated that stress corrosion cracking in tarnish-forming solutions occurs by applying a stress after the tarnish film had formed on a stress-free specimen. They also showed that the depth of the crack did not increase with length of immersion, after 30 minutes, indicating that the thickness of the tarnish film did not increase significantly with time after 30 minutes of immersion.

Forty and Humble advocate a mechanism of transgranular cracking which follows formation of a passive, brittle

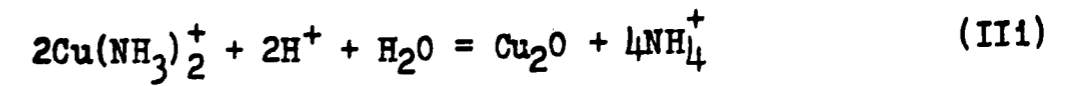
layer (Cu_2O) and the breaking of the film by yielding of the underlying metal.

McEvily and Bond¹³ have further developed the Forty and Humble model to conclude that in tarnishing solutions a cuprous oxide protective film is quickly formed. This film reduces the overall corrosion to a low level and subsequent cracking of the film exposes a small area of bare metal which is anodic to the film. Rapid anodic attack of the bare metal regenerates the protective film. The rate of thickening of the film is diffusion controlled, until a thickness is reached that cannot support the applied stress and a crack again forms, whose propagation is impeded by the newly exposed metal.

Therefore, the models of Hoar and Booker and McEvily and Bond provide two different mechanisms for tarnish formation, one an anodic reaction of the "activated" copper in a porous structure^{11,12,14,16} and the other involving a solid-state diffusion controlled cathodic reaction^{5,13}.

Ellipsometry studies¹⁷ have shown that the rate of tarnish formation is linear and diffusion is not rate controlling.

From the linear kinetics and the observation that the oxide film is not passive during anodic polarization, Green et al.¹⁷ concluded that the oxide growth involves the anodic dissolution of metal ions at the base of pores by reactions of the type given in IIa and IIg and subsequent cathodic deposition at the oxide surface by a reaction of the type given in III.



To summarize, in ammonia solutions which do not cause tarnishing, stress corrosion cracking is thought to be an anodic dissolution mechanism^{5,6,7,9,11} with continuous crack advance.

In ammonia solutions, which cause a tarnishing film, the film has been shown^{11,12,14} to be a porous epitaxial layer of cuprous oxide, which is void of zinc, and the mechanism of tarnish formation has been shown¹⁷ not to be solid-state diffusion controlled, but one of anodic pore reactions with possible cathodic reaction of the aqueous copper (II)^{11,12,14,16,17}. In tarnishing solutions, no conclusive proof of continuous^{11,14,16} or discontinuous^{5,9,12,13,15} stress corrosion crack advance has been shown.

III. EXPERIMENTAL

A. Materials

1. Brass

The brass used in this study was Olin Cartridge Brass, CDA Alloy #260, taken directly from a commercial line.

The specifications on the composition are:

Copper-----68.5-71.5%

Lead-----less than 0.007%

Iron-----less than 0.05%

Others-----less than 0.15%

Zinc-----balance.

The brass, as received, was one-inch hot-rolled plate that had been pickled to remove hot rolling scale and subsequently cold-rolled 75% to 0.64 centimeters thick.

The plate was cut into 2.54 x 2.54 x 0.64 centimeter pieces using a band saw. A notch 1.4 centimeters long and 0.25 centimeters wide was then cut into one edge of the squares with the band saw. The base of the notch was extended another 0.16 centimeters with a jeweler's hand saw using a #03 blade, which gave a notch 0.04 centimeters wide.

Specimens were notched in the rolling and transverse directions. No difference in test results was found between the specimens notched in the rolled and transverse directions.

The 2.54 centimeter square notched pieces of brass were used as the test specimens in this study.

2. Test Solution

The ammoniacal test solution, which gave tarnishing, was prepared by dissolving 8 grams of electrolytic copper dust in 1 liter of oxygenated 15N aqueous ammonia. This solution was chosen because it had been used in prior stress corrosion studies^{9,17,19} and stress corrosion cracks propagate at an appropriate rate. The 15N ammoniacal solution with 8 grams/liter dissolved copper is designated solution No. 1.

3. Chemicals

The chemicals used are listed in Appendix 1. This list gives the purity, manufacturer, and where pertinent, the density of the chemicals. All the chemicals were used without further purification.

B. Sample Preparation

A brass specimen prepared as described in Chapter III-A-1 was stressed with a titanium wedge until plastic deformation from the applied stress became evident at the base of the notch. As will be shown in Chapter IV-C the titanium wedge had no effect on corrosion potential or on crack growth rate. The specimen was washed with acetone and dried for several minutes in an oven at 30°C. The external surfaces of the specimen were coated with Tygon K-38 coating and the specimen totally immersed in a 150 milliliter beaker containing 75 milliliters of solution No. 1, which had been oxygenated for 15 minutes by slowly bubbling oxygen through the solution. The beaker was covered with parafilm.

The specimen was periodically checked for cracking and when the stress corrosion crack had progressed for a distance of 0.48 centimeters (1-1½ hours) the specimen was removed from the beaker and placed immediately in a flask of liquid nitrogen. The specimen with the entrained liquid frozen in the stress corrosion crack was broken into two pieces along the stress corrosion crack and both pieces returned to the liquid nitrogen before reaching the melting temperature of the frozen liquid.

Therefore, the entrained liquid in the growing stress corrosion crack was not only isolated from the surrounding bulk solution but the reaction within the crack was halted.

This technique for isolating the entrained liquid in a stress corrosion crack was developed by Brown et al.²⁰ for the study of stress corrosion cracking of titanium, aluminum and steel.

The entrained liquid frozen on the faces of the stress corrosion crack was removed by methods appropriate to the tests to be made on the liquid.

C. Analytical

1. Qualitative

The qualitative analysis utilized a spot test for zinc ions in the presence of copper ions^{21,22}, which gives a positive test of a reddish brown to very light purple precipitate. The reagent solution used was prepared from 8 grams of mercuric chloride and 9 grams of ammonium thiocyanate dissolved in 100 milliliters of deionized water^{21,22} and is designated as solution No. 2.

To analyze the liquid frozen on the faces of the stress corrosion crack (Chapter III-B), the solidified liquid was allowed to melt and was absorbed on a small piece of S&S, No. 589, white, quantitative grade filter paper. Several drops of solution No. 2 were dropped on the liquid absorbed on the filter paper and the filter paper was dried for 24 hours at room temperature.

The formation of a reddish brown to a very light purple precipitate which, when viewed with a microscope, had the same appearance and color as the precipitate from a control solution, was considered a positive test for zinc.

The control solution was prepared by dissolving zinc acetate in solution No. 1 to give a 15N ammoniacal solution containing 8 grams/liter dissolved copper and 3 grams/liter dissolved zinc.

2. Quantitative

The quantitative analyses used for this study were spectrophotometric methods²³ for the determination of the copper and zinc contents of a solution.

To analyze the liquid frozen to the faces of the stress corrosion crack (Chapter III-B), the liquid was allowed to melt and was picked up in a very small diameter capillary tube. The capillary tube was weighed empty and when filled with the liquid. From the weight difference of the capillary and the density for 15N ammonia the volume of liquid picked up was determined. The liquid in the capillary was transferred to 10 milliliters of a 0.1N hydrochloric acid solution, which is designated as solution No. 3.

The copper was extracted using the mixed-color method²³ given in Appendix 2 and the zinc was extracted from the remaining aqueous phase using the method²³ given in Appendix 3.

The copper and zinc extracts were diluted with carbon tetrachloride and the optical properties were determined using a Model DK-20 Beckman Spectrophotometer.

The maximum absorbance peaks at 555 millimicrons for the copper extract and at 535 millimicrons for the zinc extract were used to determine the concentrations of copper and zinc in the liquid from a stress corrosion crack.

The calibration curves for the copper and zinc were made from spectrophotometric analysis of extracts prepared, as given in Appendices 2 and 3, from control solutions. The control solutions for copper were prepared by diluting solution No. 1 with 15N ammonia to give 15N ammoniacal solutions having 6 grams/liter and 4 grams/liter dissolved copper. These solutions are designated as solutions No. 4 and No. 5 respectively. The control solutions for zinc were prepared by dissolving zinc oxide in 15N ammonia to give 15N ammoniacal solutions having 2 grams/liter, 3 grams/liter, and 4 grams/liter dissolved zinc. These solutions are designated solutions No. 6, No. 7, and No. 8, respectively.

D. pH Measurement

The pH of the frozen liquid on the faces of the stress crack (Chapter III-B) was measured by absorbing the melted liquid on a strip of narrow range pH paper. The pH paper used was pHydriion supplied by Micro Essential Laboratory, Inc. and had a range of pH 8-12 in steps of 0.5 pH units.

The pH of the bulk solution was measured with the pH paper by applying a volume of liquid similar to that from the crack sides and with a Model Zeromatic Beckman pH Meter. Although the pH of the bulk solution was found to be outside the range of the pH paper, the pH paper did provide satisfactory results for relative comparison of the pH of the crack solution and the bulk solution, as shown in Chapter IV-B.

E. Corrosion Potential

The corrosion potential of a specimen of brass in solution No. 1 was measured by soldering a piece of copper wire to the notched side of the specimen. The specimen was washed with acetone and dried for several minutes in an oven at 30°C. The solder joint and exposed copper wire were coated with Tygon K-38 in order to insulate the non-brass areas from the test solution.

The potential was determined on both stressed and unstressed specimens. Stress was induced by inserting a titanium wedge into the notch of the specimen until plastic deformation occurred at the base of the notch.

The specimen was immersed in a 150 milliliter beaker containing 100 milliliters of solution No. 1 and the corrosion potential was measured against a saturated calomel reference electrode. The voltmeter was a Precision D.C. Voltmeter #DC-100B which gives a digital read-out of the applied voltage required to zero the null meter against the voltage of the cell.

The corrosion potential was recorded for an elapsed time of up to 2½ hours.

The temperature and pH of the test solution were measured at the completion of each test.

F. Solution Electrical Conductivity

The resistance of 15N ammoniacal solutions with various concentrations of copper and/or zinc was measured using a Model 1650A General Radio Co. Impedance Bridge with 1000 cycle/second current and a dipping type conductivity cell. The cell constant for the conductivity cell was unity. All conductivity measurements were made in a 25°C constant temperature bath.

The solutions containing copper were prepared by diluting solution No. 1 with 15N ammonia to give 15N ammoniacal solutions with 2 grams/liter and 1 gram/liter dissolved copper. These solutions, which are designated solutions No. 9 and No. 10 respectively, and the solutions No. 1, No. 4, and No. 5, were used in the tests.

The solutions with zinc were prepared by adding zinc oxide to 15N ammonia to give 15N ammoniacal solutions of 1 gram/liter and 6 grams/liter dissolved zinc. These solutions, designated as solutions No. 11 and No. 12 respectively along with solutions No. 6 and No. 8 were used in the tests.

The 15N ammoniacal solutions with 8 grams/liter dissolved copper and 1 gram/liter, 2 grams/liter, 3 grams/liter and 4 grams/liter dissolved zinc were prepared by adding zinc oxide to solution No. 1.

G. Weight Loss

The corrosion rate of brass in 15N ammoniacal solution with 8 grams/liter dissolved copper was obtained by immersing a specimen in 75 milliliters of solution No. 1, which had been oxygenated for 15 minutes. The specimen was weighed, washed with acetone, and dried in an oven at 30°C for several minutes prior to immersion. At preselected times after immersion the specimen was removed from solution, rinsed with deionized water, wiped dry, and weighed to determine the weight loss.

The experimental conditions duplicated as closely as possible the conditions used in the stress corrosion studies.

IV. RESULTS AND DISCUSSION

A. Analytical

1. Qualitative

The liquid from the stress corrosion cracks was tested, as described in Chapter III-A-1, and gave positive tests for zinc in the presence of copper. The precipitate formed was crystalline and reddish brown to very light purple in color, when viewed with a microscope at 63X magnification.

These qualitative checks verified the dissolution of zinc from the brass matrix as has been proposed^{11,12,14,16,17} and gave reason to undertake quantitative analyses.

2. Quantitative

The control solutions of copper and zinc (Chapter III-C-2) were used to establish the calibration curves from which the actual concentrations of copper and zinc in the liquid in the stress corrosion cracks were determined. The results of the extractions and spectrophotometric analyses of the control solutions are shown in Tables 1 and 2 and Figures 1 and 2. The calculation procedure can be found in Appendix 4.

The liquid from the stress corrosion cracks was analyzed and the concentration of copper was found to be 14.5 grams/liter and the concentration of zinc was found to be 11.5 grams/liter, as shown in Tables 3 and 4 respectively. The calculation procedure can be found in Appendix 5. The above concentrations are average values of the concentrations found for the specimens tested and were used because the agreement between tests was better than 10%.

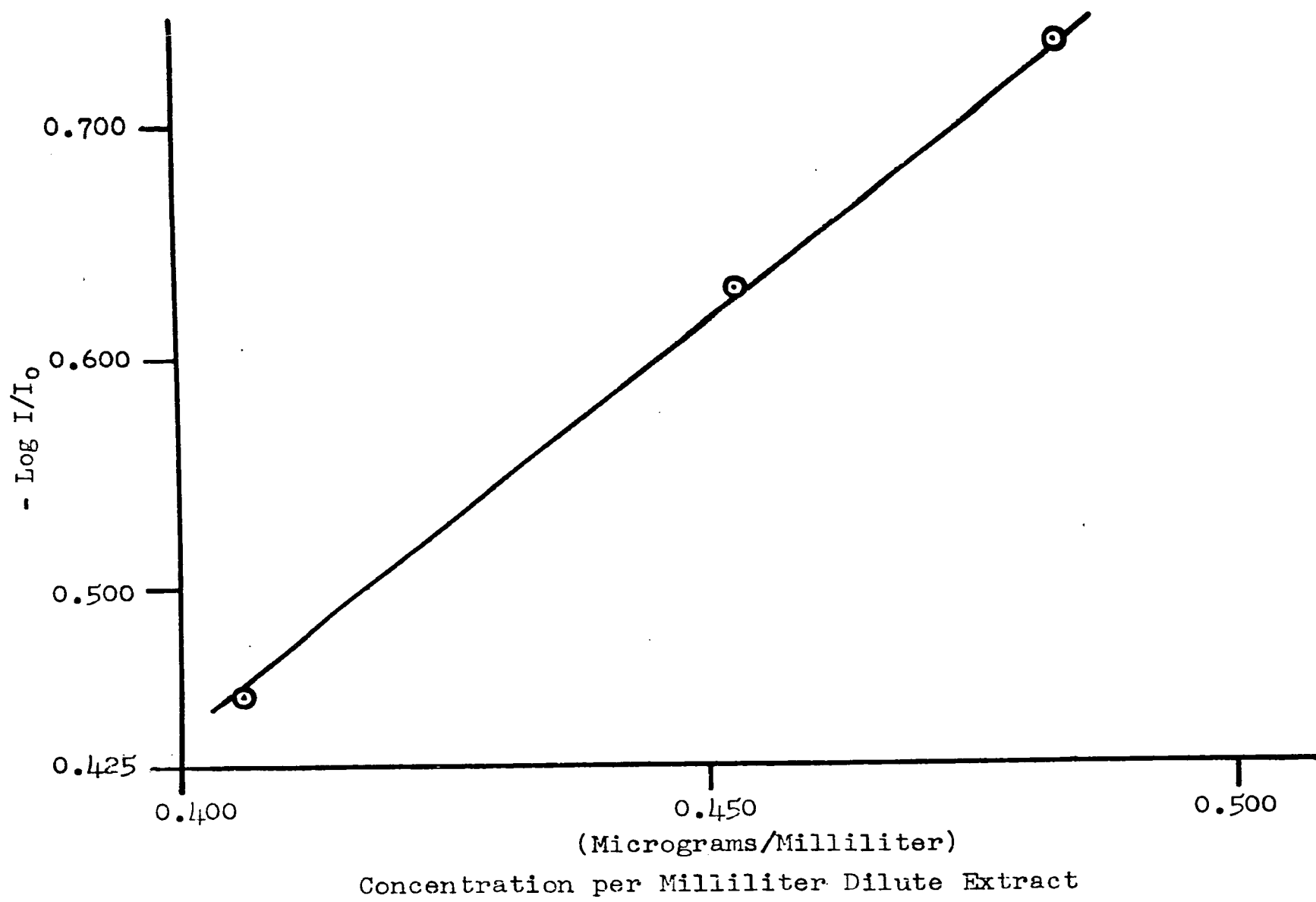


Figure 2. Calibration Curve for Zinc in 15 N Ammoniacal Solution

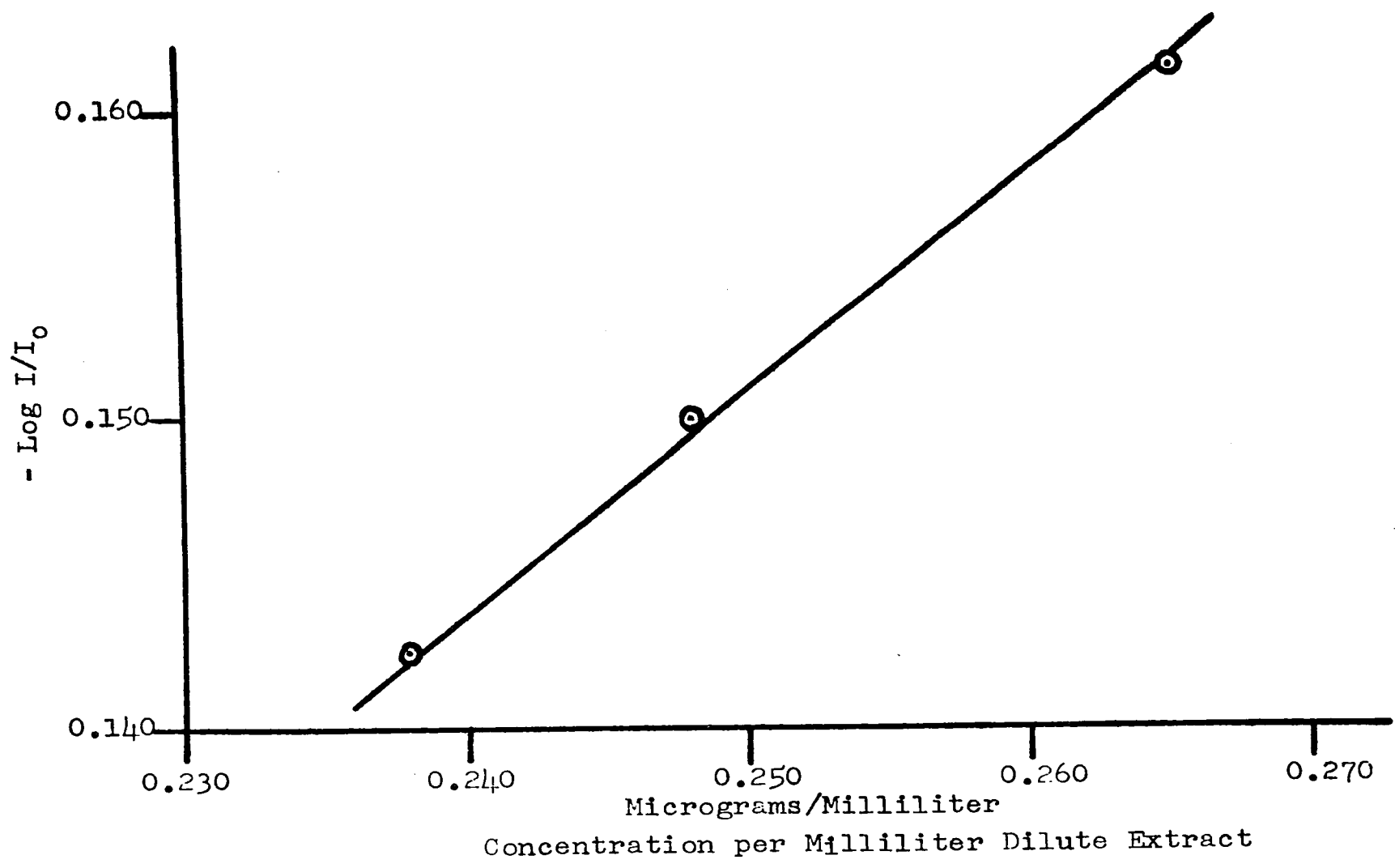


Figure 1. Calibration Curve for Copper in 15 N Ammoniacal Solution

Table 1

Spectrophotometric Analysis of Copper in Control Solutions

Solu- tion No.	Copper Conc. in Dilute Extract (γ /ml)	I_0 (%)	I (%)	$-\log I/I_0$
No. 1	0.265	95.4	65.9	0.1615
No. 4	0.238	95.4	68.7	0.1425
No. 5	0.248	95.4	67.8	0.1499

Table 2

Spectrophotometric Analysis of Zinc in Control Solutions

Solu- tion No.	Zinc Conc. in Dilute Extract (γ /ml)	I_0 (%)	I (%)	$-\log I/I_0$
No. 8	0.483	95.0	17.6	0.7355
No. 7	0.453	95.7	22.4	0.6305
No. 6	0.406	95.7	33.6	0.4540

Table 3

The Copper Concentration of Liquid from Stress Corrosion Cracks

Test Date	I_0 (%)	I (%)	$-\log I/I_0$	Copper Conc. in Dilute Extract (γ /ml)	Copper Conc. in Crack Solution (g/l)
11-17-70	95.3	68.3	0.1445	0.2427	14.1
11-28-70	94.8	67.4	0.1482	0.2456	15.0

Table 4

The Zinc Concentration of Liquid from Stress Corrosion Cracks

Test Date	I_0 (%)	I (%)	$-\log I/I_0$	Zinc Conc. in Dilute Extract (γ /ml)	Zinc Conc. in Crack Solution (g/l)
11-17-70	95.6	18.9	0.7045	0.4730	10.8
11-28-70	95.3	20.8	0.6615	0.4615	12.1

The quantitative results show that the increase in the copper content of the crack solution over the original concentration of the bulk solution is not in the 70:30 ratio of the brass composition and is consistent with the formation of a Cu_2O tarnish film^{11,12,14}.

B. pH Measurement

The pH of the liquid in stress corrosion cracks was estimated to be between pH 10.5 and pH 11.0, when measured as described in Chapter III-D. The pH of the 15N ammoniacal solution was found to be pH 11.0, when measured with the pHDrion paper.

Although measurement of the pH of the 15N ammoniacal solutions with the Beckman pH Meter gave a pH 13.8 and the pH read pH 11.0, the difference is most likely due to the small volume of liquid which wetted the paper. When the pH paper was dipped into the bulk solution, the paper read the maximum of pH 12.0.

The significance of the pH measurement is the evidence that the pH of the crack solution and the pH of the bulk solution are essentially the same.

C. Corrosion Potential

The corrosion potential for the cell



where M is the brass and M^{++} is copper and zinc ions in solution is given by the equation IVa²⁴.

$$E^{\circ} = E^{\circ}_{KCl_{(sat.)};Hg_2Cl_2,Hg} - E^{\circ}_{M^{++};M} \quad (IVa)$$

The potential of the calomel electrode, $E^{\circ}_{KCl_{(sat.)};Hg_2Cl_2,Hg}$, is taken as 0.2415 volts at 25°C²⁵. The temperature correction factor is 0.00076 (T-25°C)²⁴, which gives the corrected potential from equation IVb.

$$E^{\circ}_{KCl_{(sat.)};Hg_2Cl_2,Hg} = 0.2415 - 0.00076 (T-25^{\circ}C) \quad (IVb)$$

The potential for the above cell is shown in Figure 3. From these curves it can be seen that there is no apparent effect of the titanium wedge on the potential. This observation gives a good basis for assuming that the use of a titanium wedge did not affect the chemistry of the stress corrosion process.

The initial potential and the pH (Chapter IV-B) in each case are such as to fall in the Cu_2O region of the superimposed Pourbaix diagrams for copper and in the soluble $Zn(NH_3)_4^{2+}$ region for zinc in 15N ammonia (Figure 4), as calculated from the equation of Johnson and Leja²⁶. These calculations are found in Appendix 6. The potential drifts with time and approaches the boundary that separates the Cu_2O , CuO , $Cu(NH_3)_4^{2+}$ and $Cu(NH_3)_2^{\dagger}$ regions.

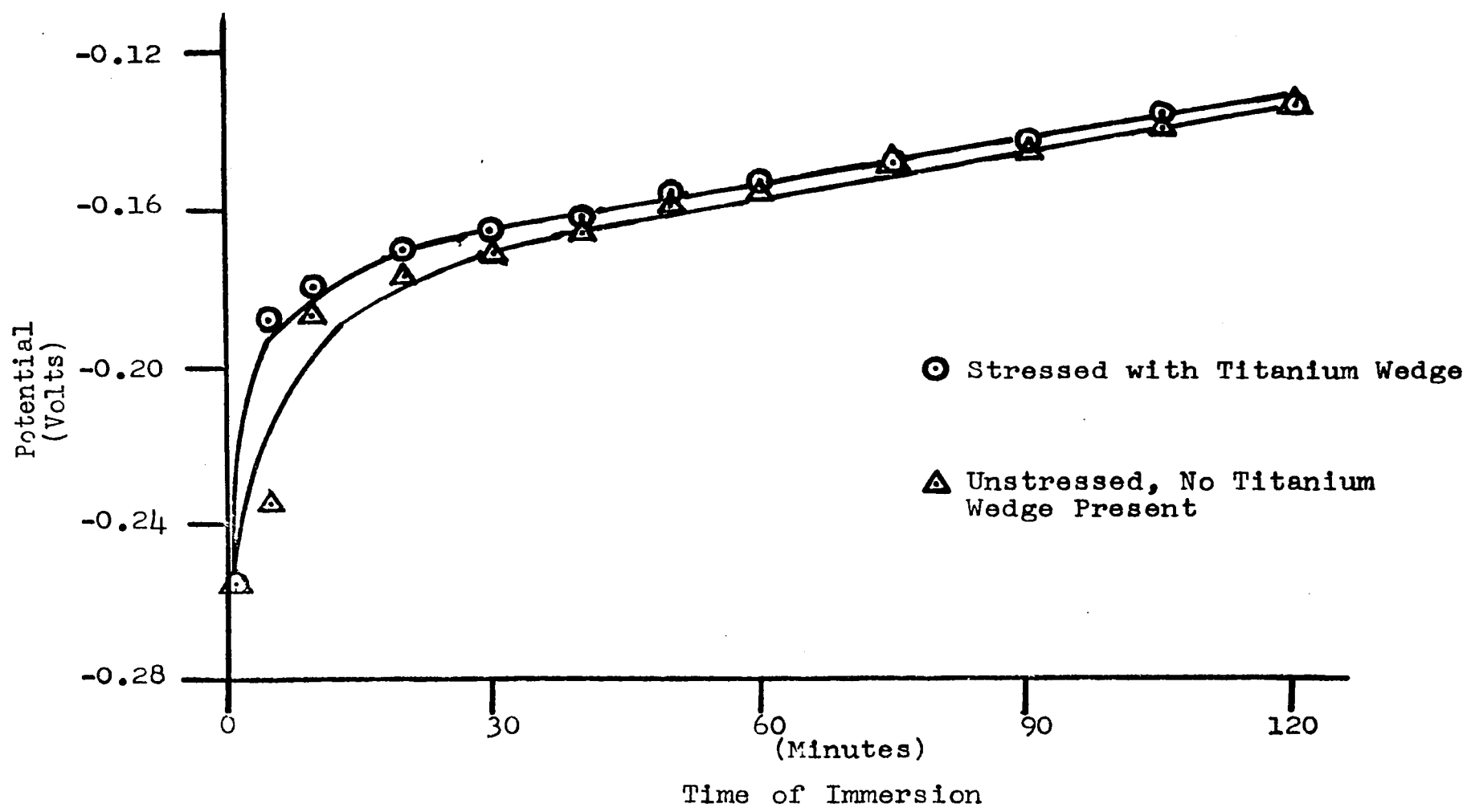


Figure 3. Corrosion Potential for Brass Specimens in 15 N Ammoniacal Solution With 8 Grams/Liter Dissolved Copper

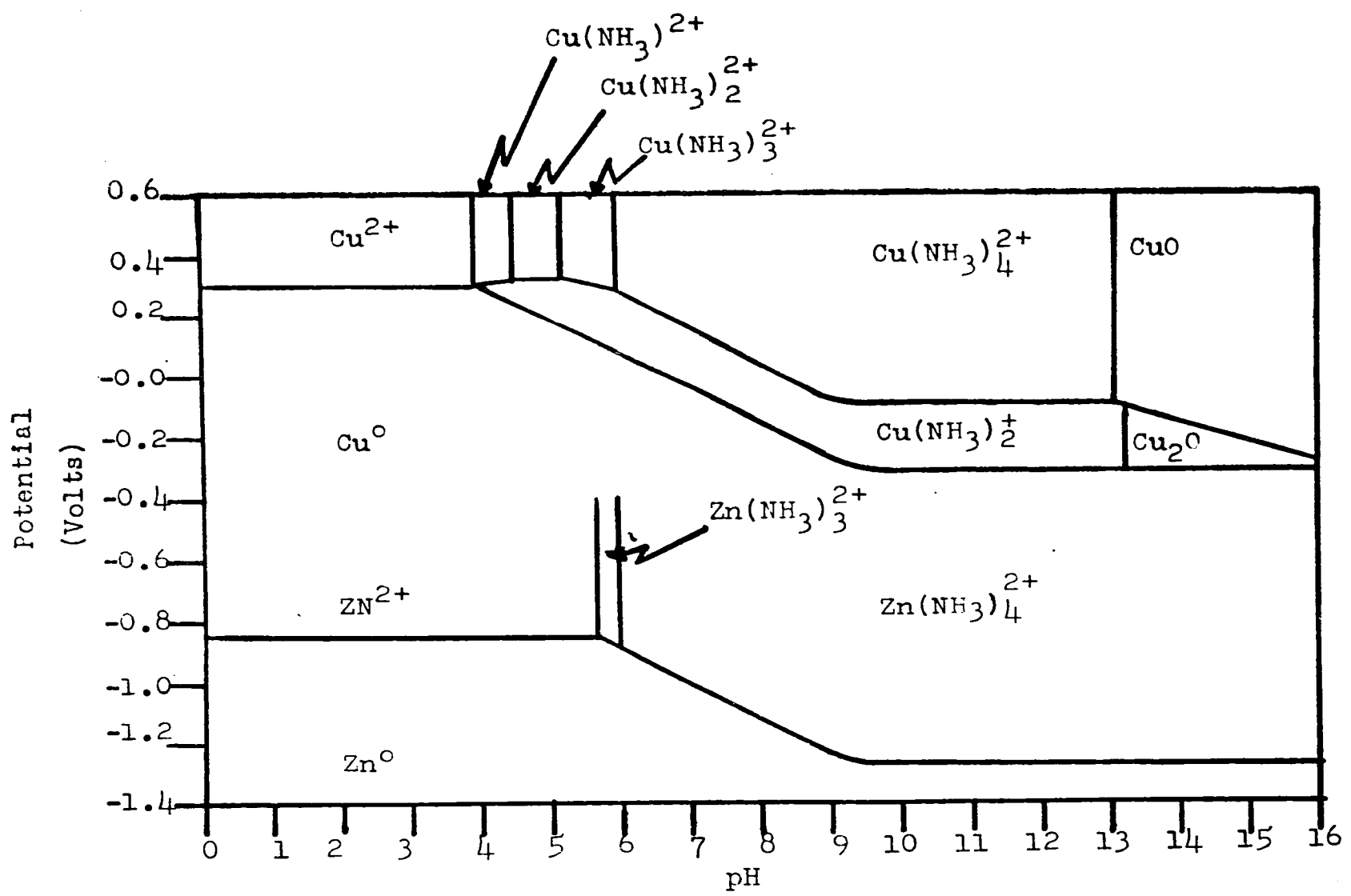


Figure 4. Superimposed Pourbaix Diagrams of Copper and Zinc in 15 N Ammoniacal Solution with 8 Grams/Liter Dissolved Copper

D. Solution Electrical Conductivity

The electrical conductivity of 15N ammoniacal solutions increases with increase in metal ion concentration as shown in Figures 5 and 6. The increase in conductivity, or decrease in resistivity, provides a continually improving path for a cathodic-anodic reaction couple in the stress corrosion crack as corrosion and dissolution of metal occurs.

E. Weight Loss

The weight loss in grams/square centimeter is plotted against time of immersion in Figure 7.

The weight loss was linear with time. A rate of corrosion of 5.39×10^{-6} gram/square centimeter/minute is in good agreement with the rate of weight loss, 1.25×10^{-6} grams/square centimeter/minute, for copper reported by Jenkins and Durham²⁷. However, it is lower than the 6.3×10^{-5} grams/square centimeter/minute reported by Pugh and Westwood¹⁹ who used a stirred solution. The stirring increases the weight loss because the diffusion limited reaction increases in rate as oxygen is brought to the surface of the sample.

The dissolution rate for copper and zinc in a stress corrosion crack was calculated from the spectrophotometrically determined concentrations of copper and zinc. The assumptions necessary for the calculations are:

1. Crack solution volume 5 microliters.
2. Linear crack growth over a 60 minute period and a 30 minute period.
3. Final crack surface 0.61 square centimeters; therefore,

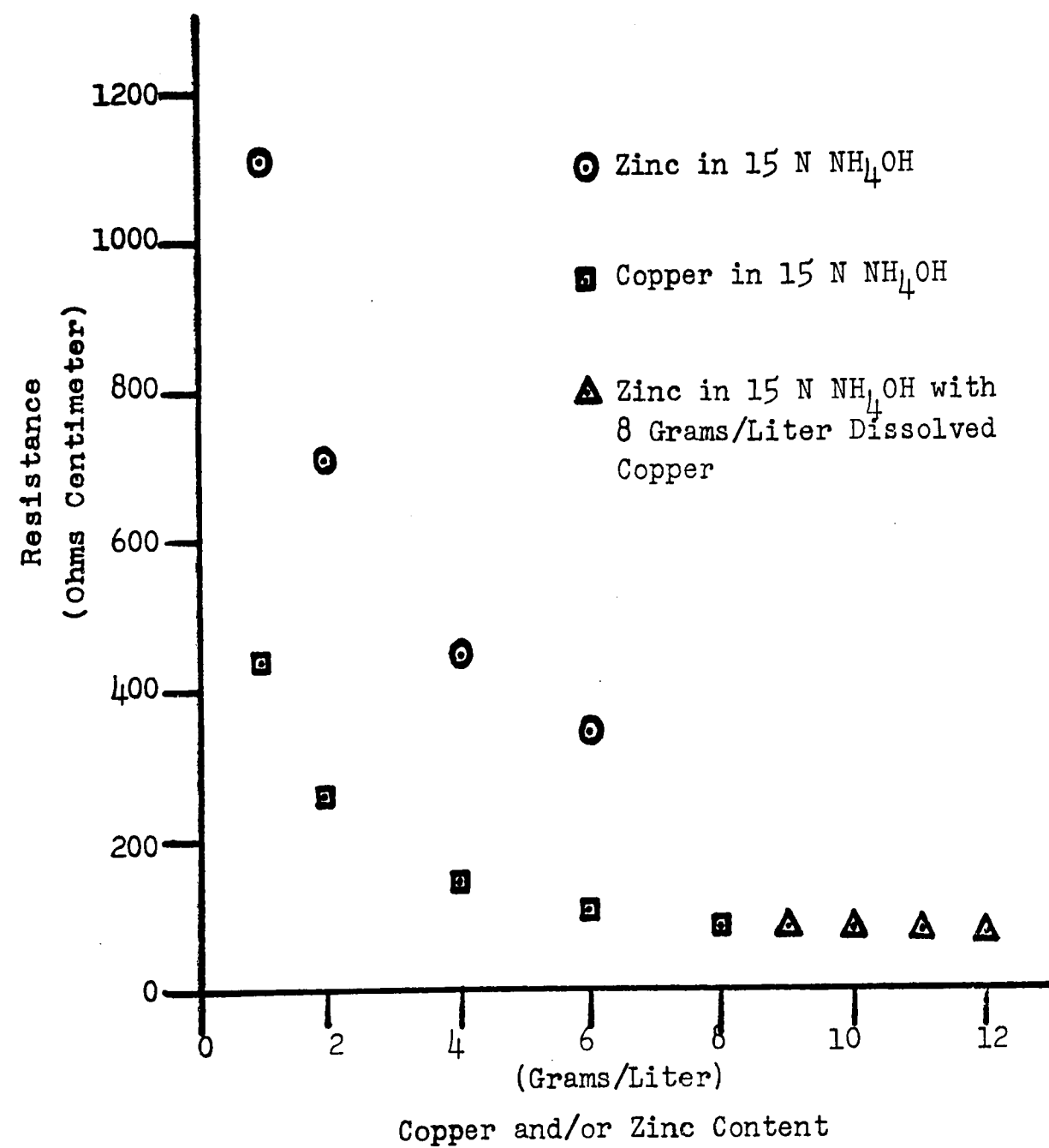


Figure 5. Electrical Resistance of 15 N Ammoniacal Solutions with Various Concentrations of Dissolved Copper and/or Zinc

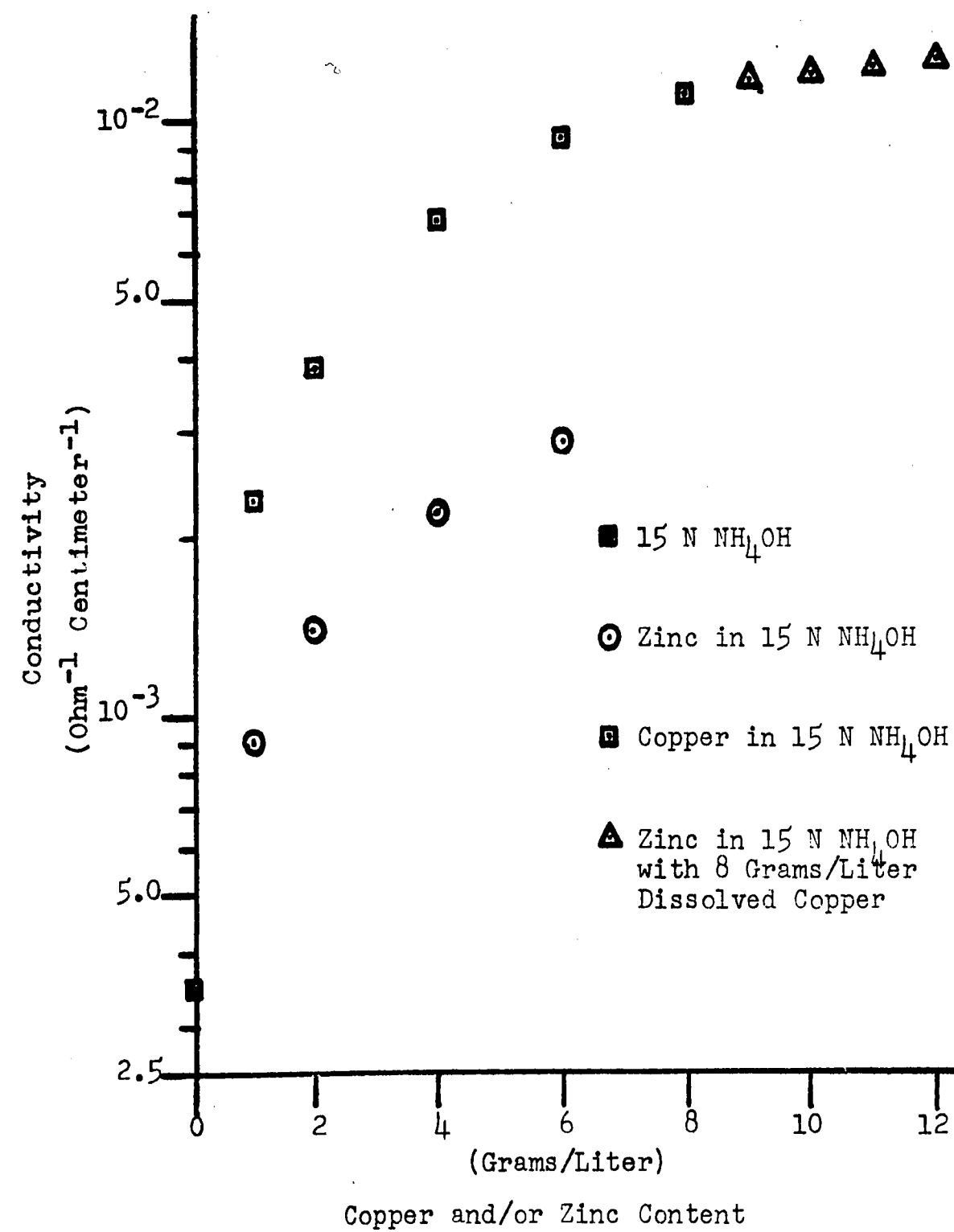


Figure 6. Electrical Conductivity of 15 N Ammoniacal Solutions with Various Concentrations of Dissolved Copper and/or Zinc

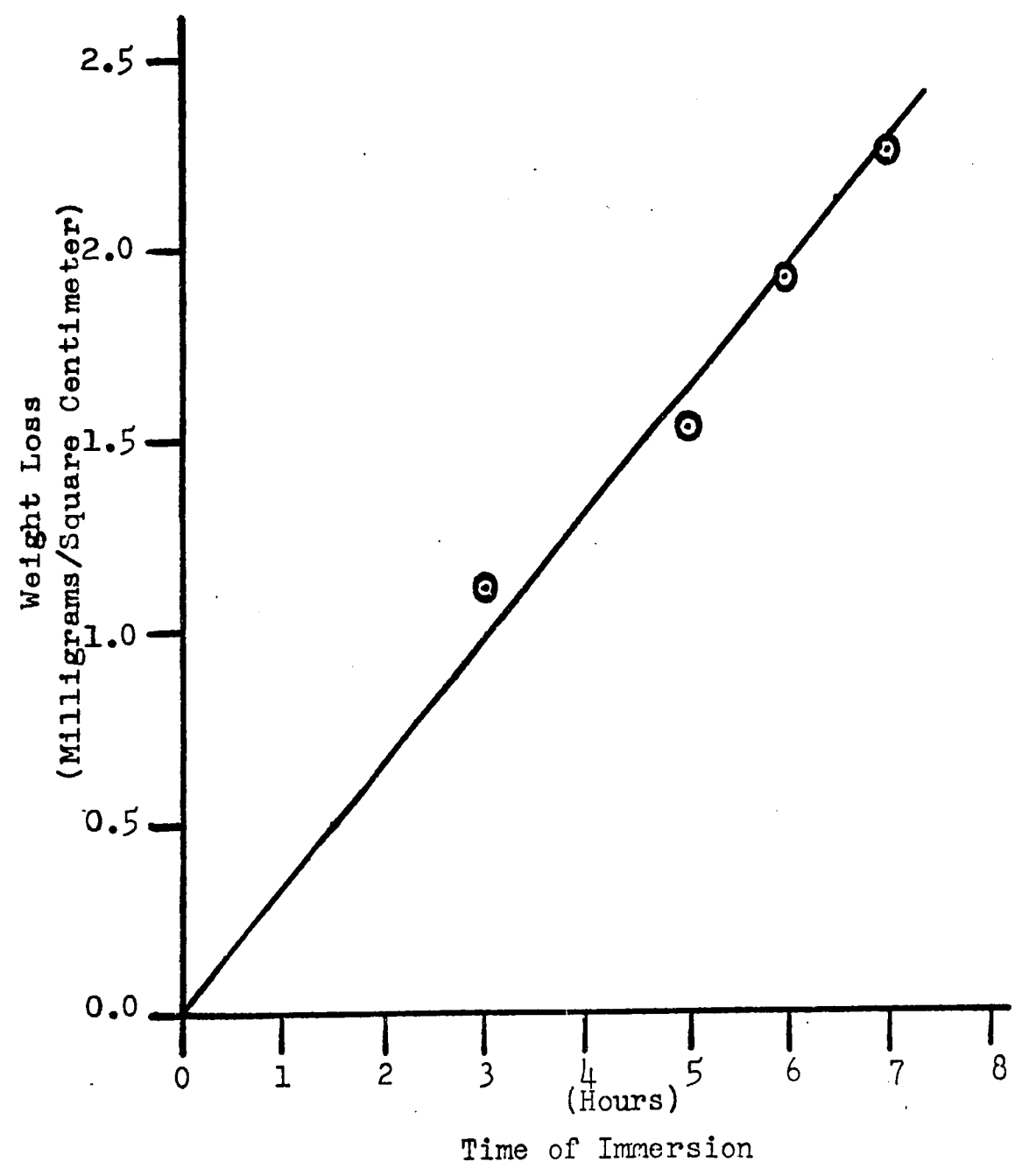


Figure 7. Weight Loss from Brass in 15 N Ammoniacal Solution with 8 Grams/Liter Dissolved Copper

the dissolution rate within the crack was 4.14×10^{-6} grams/square centimeter/minute for 60 minutes of linear crack growth and 7.35×10^{-6} grams/square centimeter/minute for 30 minutes of linear crack growth.

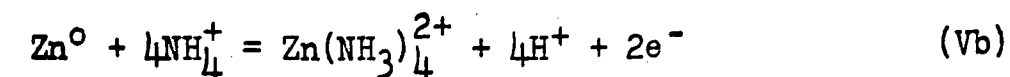
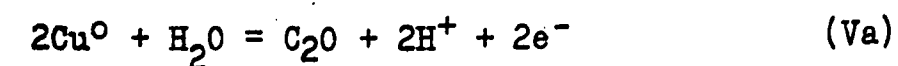
The fact that the dissolution rate within the crack was approximately the same as the dissolution rate for the specimen as a whole suggests that the crack is not anodic to the external surfaces of the specimen. Therefore, any significant electrochemical reaction with appreciable separation of the anodic and cathodic areas must be confined to the internal surface of the crack.

V. SUMMARY AND CONCLUSIONS

Dissolution of both copper and zinc occurs within a growing stress corrosion crack in 70:30 brass (CDA Alloy #260) immersed in 15N ammonium hydroxide containing 8 grams/liter dissolved copper. The copper and zinc concentrations observed near the crack tip were 14.1 grams/liter copper and 11.5 grams/liter zinc after immersion for 1½ hours. The relative dissolution rates of copper and zinc from the brass matrix were thus in a 35:65 ratio as compared to the 70:30 ratio of the elements in the alloy. Preferential dissolution of zinc (dezincification) occurred within the crack.

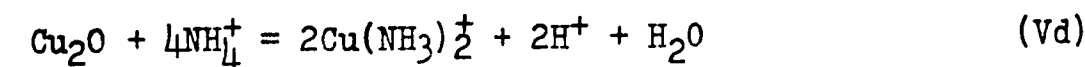
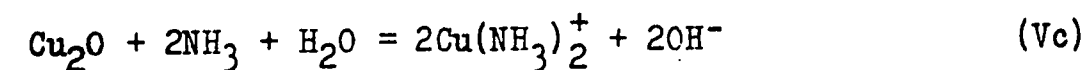
These results are consistent with the behavior to be expected from consideration of the superimposed Pourbaix diagrams for copper and zinc. At the corrosion potential of -0.145 volts and a pH of 13.3, the thermodynamically favored corrosion products are $\text{Zn}(\text{NH}_3)_4^{2+}$, $\text{Cu}(\text{NH}_3)_2^+$ and cuprous oxide. The presence of cuprous oxide was confirmed by visual appearance and the presence of the soluble $\text{Zn}(\text{NH}_3)_4^{2+}$ and $\text{Cu}(\text{NH}_3)_2^+$ was confirmed by the increase in the concentration of the metals in the solution within the crack.

The observations made in this study are consistent with the following mechanism for the stress corrosion cracking of brass in concentrated ammonium hydroxide containing 8 grams/liter dissolved copper. The primary anodic reactions leading to the formation of Cu_2O and $\text{Zn}(\text{NH}_3)_4^{2+}$ are those of Hoar and Bocker¹¹, equations Va and Vb.



The fact that the Cu_2O is formed in a primary reaction and not as a secondary reaction from species in solution finds confirmation in the observations of Forty and Humble¹² and Johnson and Leja⁸ that the tarnish penetrates the brass substrate and is not loosely deposited on the surface.

It is further proposed that the increased amount of soluble copper species found in the crack solution is a consequence of a rate-controlling dissolution of Cu_2O by either of the reactions¹⁹ Vc or Vd.



The fact that the dissolution rate within the crack was approximately the same as the dissolution rate for the specimen as a whole suggests that the crack is not anodic to the external surface of the specimen. Any significant electrochemical reaction with appreciable separation of the anodic and cathodic areas must be confined to the internal surface of the crack.

It is hypothesized that the stress corrosion cracking of brass in concentrated ammonia solutions is simply a consequence of the preferential dissolution of zinc from the brass matrix with weakening of the matrix at the crack tip where the stress concentration is the highest.

In conclusion, this study has:

1. Provided a workable analytical procedure for the quantitative analysis of the liquid within a growing stress corrosion crack.
2. Provided experimental evidence to support a mechanism in 15N ammoniacal solutions of anodic dissolution of zinc at the crack tip, with anodic oxidation of the copper remaining in the matrix to Cu_2O , and the subsequent cathodic dissolution of the surface Cu_2O .
3. Shown that the pH of the crack solution does not vary significantly from that of the bulk solution.
4. Suggested that the stress corrosion cracking of brass in concentrated ammonium hydroxide solution results from preferential dissolution of zinc with weakening of the matrix at the crack tip where the stress concentration is highest.

Appendix 1

The following is a list of all the chemicals used in this study.

<u>Chemical</u>	<u>Grade</u>	<u>Supplier</u>	<u>Density</u>
Acetone	Reagent	Lehigh Valley Chemical Co.	
Ammonium Hydroxide	Reagent	Lehigh Valley Chemical Co.	0.90 g/ml
Ammonium Sulfate	Certified	Fisher Scientific Co.	
Ammonium Thiocyanate	Certified	Fisher Scientific Co.	
Bromocresol Green Solution 0.04%	Certified	Fisher Scientific Co.	
Carbon Tetrachloride	Reagent	Lehigh Valley Chemical Co.	1.58 g/ml
Copper Metal (Electrolytic Dust)	Purified	Fisher Scientific Co.	
Cupric Sulfate	Reagent	J. T. Baker Chemical Co.	
Diphenyl Thiocarbazon (Dithizone)	C.P.	Fisher Scientific Co.	
Hydrochloric Acid	Reagent	Corco Chemical Corp.	1.19 g/ml
Mercuric Chloride	Reagent	J. T. Baker Chemical Co.	
Methanol	Reagent	Lehigh Valley Chemical Co.	
Sodium Acetate	Reagent	J. T. Baker Chemical Co.	
Sodium Sulfide	Reagent	J. T. Baker Chemical Co.	
Sodium Thiosulfate	Reagent	Lehigh Valley Chemical Co.	
Zinc Acetate	Reagent	J. T. Baker Chemical Co.	
Zinc Oxide	Reagent	J. T. Baker Chemical Co.	

Appendix 2The Dithizone Method of Copper Determination

The mixed-color method²³ for the determination of copper was used for this study.

The mixed-color method reacts copper in 0.1N hydrochloric acid with dithizone in carbon tetrachloride to form the keto complex. Zinc does not react appreciably in 0.1N hydrochloric acid unless present in high concentrations.

Reagents

Dithizone, 0.001% solution by weight in carbon tetrachloride.

Hydrochloric Acid, 0.1N prepared with deionized water.

Procedure

After the liquid from a stress corrosion crack had been transferred to 10 milliliters of 0.1N hydrochloric acid in a small separatory funnel the 0.001% dithizone is added in 1-2 milliliter quantities. After each addition, the solution is shaken for 2 minutes and if the dithizone changes in color the carbon tetrachloride phase is delivered to a suitable vessel. When the last addition of dithizone remains unchanged, it is delivered to the previous extracts.

The transmittancy of the keto copper dithizonate with excess dithizone present, diluted with carbon tetrachloride, is obtained at 555 millimicrons.

Appendix 3The Dithizone Method of Zinc Determination

The mono-color method²³ for the determination of zinc was used for this study.

The mono-color method reacts zinc in a slightly acid solution with dithizone in carbon tetrachloride to form zinc dithizonate. Sodium sulfide is added to remove excess dithizone. Any copper present is complexed with sodium thiosulfate to prevent its reaction with dithizone.

Reagents

Dithizone, 0.005% solution by weight in carbon tetrachloride.

Sodium Acetate Solution, 0.5M prepared with deionized water.

Free the solution of heavy metals by shaking small portions of 0.005% dithizone and filter through a small moistened filter paper to remove droplets of carbon tetrachloride.

Sodium Thiosulfate Solution, 50 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is dissolved in 100 milliliters of deionized water.

Sodium Thiosulfate-Acetate Wash Solution, Mix 225 milliliters of 0.5M sodium acetate solution, 10 milliliters of 50% sodium thiosulfate solution, 40 milliliters of 10% nitric acid, and add deionized water to make 500 milliliters.

Free the solution of heavy metals as described above.

Sodium Sulfide Wash Solution, Dilute 40 milliliters of a 1% sodium sulfide with 1 liter of deionized water.

Procedure

The aqueous phase remaining after the extraction of copper from the 0.1N hydrochloric acid solution is adjusted to pH 5-5.5 with sodium acetate solution using bromocresol green indicator. A small amount of sodium thiosulfate solution is added to complex any copper which may have remained. Shake the solution with 2-3 milliliters of 0.005% dithizone and draw extract off into another small separatory funnel. Repeat the extraction until the last portion of dithizone remains unchanged in color after shaking 2-3 minutes.

Wash the combined carbon tetrachloride extracts two times with 5 milliliter portions of sodium thiosulfate-acetate wash solution. Wash once with deionized water, and with 5 milliliter portions of sodium sulfide solution until the last wash remains colorless.

Dilute the zinc dithizonate solution with carbon tetrachloride and obtain the transmittancy at 535 millimicrons.

Appendix 4Calculation ProcedureFor the Calibration Curves of Copper and Zinc

The calculation procedure will be described for the copper calibration curve with reference to Table 5 of this appendix. The same procedure can be applied to Table 6 to determine the calibration curve for zinc.

Procedure

The weight of the empty capillary, column 2, is subtracted from the weight of the full capillary, column 1, to get the weight of the control solution, column 3. The weight of the control solution, column 3, is divided by the density of the control solution, which is taken to be that of 15N ammonia (0.90 g/milliliter) and the resulting volume of the control solution is recorded in column 4. The weight of copper in the control solution, column 5, is found by multiplying column 4 by the concentration of the control solution in grams/milliliter. The weight of copper, column 5, is divided by the volume of the extract, column 6, to find the copper concentration of the extract, column 7. Column 8 is the dilution ratio of the extract and when multiplied by column 7 gives the copper concentration of the dilute extract, column 9. Columns 10 and 11 are the intensities of the solvent (CCl_4) and the control solution extract as taken from the spectrophotometric analysis and column 12

Table 5

Data and Calculated Values for Construction of Spectrophotometric Calibration Curve for Copper

Control Solution No.	Column											
	1 (g)	2 (g)	3 (g)	4 (ml)	5 (γ)	6 (ml)	7 (γ /ml)	8	9 (γ /ml)	10 (%)	11 (%)	12
1	0.00780	0.00550	0.00230	0.00255	20.140	12.85	1.587	5:1	0.265	95.4	65.9	0.1615
4	0.00771	0.00494	0.00277	0.00308	18.48	12.95	1.427	5:1	0.238	95.4	68.7	0.1425
5	0.00855	0.00652	0.00203	0.00225	9.00	6.05	1.487	5:1	0.248	95.4	67.8	0.1499

Table 6

Data and Calculated Values for Construction of Spectrophotometric Calibration Curve for Zinc

Control Solution No.	Column											
	1 (g)	2 (g)	3 (g)	4 (ml)	5 (γ)	6 (ml)	7 (γ /ml)	8	9 (γ /ml)	10 (%)	11 (%)	12
8	0.02150	0.01700	0.00450	0.00500	20.00	4.6	4.348	8:1	0.484	95.0	17.6	0.7355
7	0.02544	0.02146	0.00398	0.00442	13.2	3.25	4.080	8:1	0.453	95.7	22.4	0.6305
6	0.02396	0.02085	0.00411	0.00457	9.2	2.5	3.656	8:1	0.406	95.7	33.6	0.4540

is the negative logarithm of the ratio of column 11 to column 10.

The calibration curve is drawn from a plot of column 9 against column 12.

Appendix 5Calculation Procedure to Determine the Copper and Zinc Concentration of the Stress Corrosion Crack Solution

The calculation procedure will be described for the copper in the solution with reference to Table 7 of this appendix. The same procedure is applied to Table 8 to determine the zinc concentration.

Procedure

The weight of the empty capillary, column 2, is subtracted from the weight of the full capillary, column 1, to get the weight of crack solution, column 3. The weight of crack solution, column 3, is divided by the density of the crack solution, which is taken to be that of 15N ammonia (0.90 grams/milliliter) and the resulting volume of crack solution is recorded in column 4. Columns 5 and 6 are the intensities of the solvent (CCl_4) and the crack solution extract as taken from the spectrophotometric analysis and column 7 is the negative logarithm of the ratio of column 6 to column 5. Column 8 is the concentration of copper per milliliter of dilute extract as read from the calibration curve and column 9 is the dilution ratio of the extract. Multiplying column 8 and 9 gives the concentration of copper per milliliter of extract, column 10. Column 11 is the volume of extract (Chapter III-C-2) and when multiplied by column 10 gives the total weight of copper, column 12, extracted from the crack solution. Column 13, the concentration of

Table 7

Data and Calculated Values for the Determination of the
Copper Concentration of Stress Corrosion Crack Solutions

Date of Test	Column						
	1 (g)	2 (g)	3 (g)	4 (ml)	5 (%)	6 (%)	7
11-17-70	0.00710	0.00589	0.00121	0.00134	95.3	68.3	0.1445
11-28-70	0.00885	0.00786	0.00099	0.00110	94.8	67.4	0.1481

Date of Test	Column						
	8 (σ /ml)	9	10 (σ /ml)	11 (ml)	12 (σ)	13 (g/ml)	14 (g/l)
11-17-70	0.2407	5:1	1.4442	13.1	18.97	0.01411	14.1
11-28-70	0.2456	7:1	1.9648	8.4	16.50	0.01500	15.0

Table 8

Data and Calculated Values for the Determination of the
Zinc Concentration of Stress Corrosion Crack Solutions

Date of Test	Column						
	1 (g)	2 (g)	3 (g)	4 (ml)	5 (%)	6 (%)	7
11-17-70	0.00710	0.00589	0.00121	0.00134	95.6	18.9	0.7045
11-28-70	0.00885	0.00786	0.00099	0.00110	95.3	20.8	0.6611

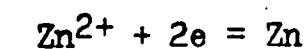
Date of Test	Column						
	8 (σ /ml)	9	10 (σ /ml)	11 (ml)	12 (σ)	13 (g/ml)	14 (g/l)
11-17-70	0.4730	8:1	4.2570	3.4	14.47	0.01080	10.8
11-28-70	0.4615	11:1	5.5538	2.4	13.29	0.01208	12.1

copper per milliliter of crack solution, is obtained by dividing column 12 by column 4 and column 14 is the result of expressing column 13 in grams/liter.

Appendix 6Sample CalculationsFor the Pourbaix Diagrams of Copper and Zinc

The calculations for the Pourbaix diagrams of zinc and copper are based on the equations and constants given by Johnson and Leja²⁶ and follow the conventions of Pourbaix²⁸ for setting up the equation. The concentration of Zn^{2+} was taken as 0.001M and the concentration of NH_3 and NH_4^+ was taken as 15M.

A typical equation to define the potential boundary between two regions of the zinc diagram and the calculation using that equation is as follows:

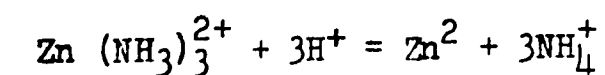


$$E = -0.763 + 0.0295 \log [Zn^{2+}]$$

$$E = -0.763 + 0.0295 \log 0.001$$

$$E = -0.851$$

The other typical equation defines the pH at which the equilibrium between compounds, dependent only on the pH of the solution, will occur and is as follows:



$$pH = 6.83 + 0.333 \log [Zn(NH_3)_3^{2+}] / [Zn^{2+}] - \log [NH_4^+]$$

where at equilibrium between Zn^{2+} and $Zn(NH_3)_3^{2+}$,

$$[Zn^{2+}] = [Zn(NH_3)_3^{2+}]$$

Therefore,

$$\text{pH} = 6.83 + 0.333 \log 1.0 - \log 15.0$$

$$\text{pH} = 5.65.$$

The calculations for the Copper Pourbaix diagram are of the same type as shown for zinc and were made with the concentration of Cu^{2+} taken as 0.126M and concentration of NH_3 and NH_4 taken as 15M.

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Vita

Mr. Roy H. Kissinger was born in Dallastown, Pennsylvania on June 6, 1941, the first child of Mr. and Mrs. Boyce F. Kissinger. He attended public grammar and high school in Dallastown, Pennsylvania. He has received the degree of Associate of Science from York Junior College, York, Pennsylvania in 1961, and the degree of Bachelor of Science in Chemical Engineering from Bucknell University, Lewisburg, Pennsylvania, in 1963. He then spent six years in the chemical and book manufacturing industries, after which he entered graduate studies at Lehigh University in September, 1969. While at Lehigh University, he held a Research Assistantship sponsored by the International Copper Research Association, Inc.

Mr. Kissinger is married to the former Lori Ann Border and is the father of one daughter, Mignonne Ann.