CORROSION OF METALS IN AQUEOUS SOLUTIONS

By

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CORROSION OF METALS IN AQUEOUS SOLUTIONS

Summary

This project was undertaken to investigate the feasibility of the following experiments:

(a) The illustration of the displacement of an ion in solution by a more active metal as predicted by the electromotive series.

(b) The demonstration of the driving force in galvanic corrosion or the potential developed in a couple of dissimilar metals.

(c) The demonstration of the influence of cathode area on the magnitude of galvanic corrosion.

(d) The demonstration that an ion concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal in contact with the solution of different concentrations.

(e) The demonstration that an oxygen concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

(f) The demonstration of the corrosion resistance and nobility of iron when in the passive condition.

(g) The demonstration of the passivation of steel in oxidizing environments by alloying it with chromium or chromium and nickel.

(h) The demonstration of the active and passive electrode potentials of stainless steel.

These experiments were set up by the International Nickel Company as outlined in their report "Corrosion in Action." The present investigation was concerned with the feasibility and limitations of these experiments. If feasible, these experiments were to be used in the future as laboratory exercises for undergraduate Metallurgy and Chemical Engineering students.

Each experiment was performed as outlined in the report with only a few minor changes. Some of the metals which were called for in the report could not be obtained. Particular interest was paid to the length of the individual experiments and also to the deviation of the data from the original data. The data obtained for experiment (d) were the only ones that varied to a great extent from the original work.

In the present study it was found that the experiments were set up in such a way that they could be performed in a short time, and they also showed clear results. Therefore, it is believed that these experiments would be suitable as laboratory exercises which demonstrate the many causes of corrosion.

It is suggested that higher concentrations of copper sulfate solution be used in experiment (d) in order to obtain better results. It is also suggested that 3% and 6% chromium steel be obtained for experiment (g). This would help to show the necessity for at least 12 wt % chromium in solid solution with iron for passivity in aqueous oxidizing environments.

CORROSION OF METALS IN AQUEOUS SOLUTIONS

Introduction

This project was undertaken to investigate a set of experiments which were designed to demonstrate certain fundamental concepts involved in the aqueous corrosion of metals and alloys. These experiments appeared to be the type which would be appropriate for use in the future as laboratory exercises for undergraduate Metallurgy and Chemical Engineering students.

The feasibility and limitations of the following eight experiments were to be investigated:

(a) The illustration of the displacement of an ion in solution by a more active metal as predicted by the Electromotive Series.

(b) The demonstration of the driving force in galvanic corrosion or the potential developed in a couple of dissimilar metals.

(c) The demonstration of the influence of area of the cathode materials on the magnitude of galvanic corrosion.

(d) The demonstration that an ion concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

(e) The demonstration that an oxygen concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

(f) The demonstration of the corrosion resistance and nobility of iron when in the passive condition.

(g) The demonstration of the passivation of steel in oxidizing environments by alloying it with chromium or chromium and nickel.

(h) The demonstration of the active and passive electrode potentials of stainless steel.

Extensive work has been done on this subject by all of the leading producers of metals. Information on this subject can be found in the Metals Handbook and in the metallurgical and chemical literature. This project followed the work previously done by the International Nickel Company, Inc. Their work was outlined in the report "Corrosion in Action,"[1] and this outline was followed in detail.

Before discussing the experiments in detail it is profitable to consider some basic concepts of the corrosion of metals which are demonstrated by the experiments.

Some Basic Concepts of Metallic Corrosion

"The basic cause of corrosion is the instability of metals in their refined forms. Because of this free energy relationship, the metals tend to revert to their natural states through the processes of corrosion. In the case of iron the action of rain forms rust."[2] Rust is iron oxide, and therefore in rusting iron has reverted to its original native state.

The basic nature of corrosion is almost always the same - a flow of electricity between certain areas of a metal surface through a solution capable of conducting an electric current. This electrochemical action causes destructive alteration or eating away of a metal at areas which are called anodes, where the metal ions leave the metal and enter the solution. (The flow of ions in the solution constitutes the flow of electricty in the solution.)

One of the first requirements of corrosions is the presence of an electrolyte. An electrolyte is any liquid or solid that contains ions. This discussion is confined to liquid electrolytes. The corrosive environment may vary in reactivity from plain water to the strongest acid or the strongest alkali. It may simply be the moisture from the air, or it may be salt water. There must be two electrodes in the corrosion circuit, an anode and a cathode, where current enters and leaves the electrolyte. These electrodes may consist of two different kinds of metal, or they may be also different areas on the same piece of metal. There must be potential difference between the two electrodes, or areas, so that electricity will flow between

them. It is necessary to have a wire or metallic path to complete the circuit for the flow of electrons. As shown in Figure 1, the negatively charged electrons move in the wire from the negative electrode (anode) to the positive electrode (cathode).

At the anode, positively charged atoms of metal (ions) detach themselves from the solid surface and enter into solution as ions, while the corresponding negative charges, in the form of electrons, are left behind in the metal. The released electrons then travel through the metal to the cathode area. At the cathode, the electrons reaching the surface through the metal meet and neutralize some positively charged hydrogen ions which have arrived at the same surface through the electrolyte. This reaction can be shown by the following equations:

$$2H^{+} + 2e \rightarrow 2H \qquad 2H \rightarrow H_2$$

or $$2H^{+} + \tfrac{1}{2}O_2 + 2e \rightarrow H_2O \qquad \tfrac{1}{2}O_2 + H_2O + 2e \rightarrow 2\bar{O}H$$

By losing their charge, the hydrogen ions become neutral atoms again, and may combine to form hydrogen gas. The release of hydrogen ions causes an accumulation of a relatively high concentration of OH ions which are left behind to increase the alkainity at the cathode or to make the solution less acid.

For corrosion to occur, then, there must be a release of electrons at the anode, and a formation of metal ions through oxidation and disintegration of the metal. At the cathode, there must be a simultaneous acceptane of the electrons which can be caused by neutralization of positive ions or formation of negative ions.

The basic causes of corrosion shown by the experiments are described

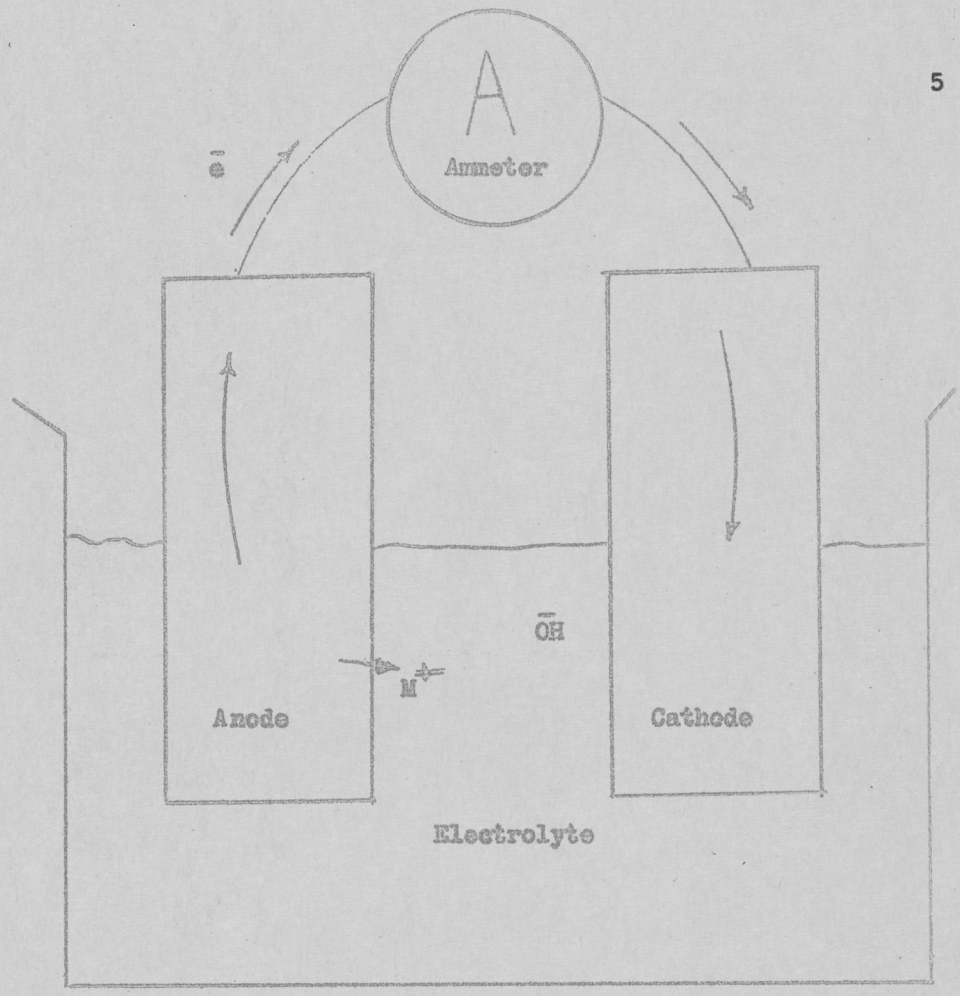


Figure 1 Schematic representation of corrosion circuit

below.

(a) The illustration of the displacement of an ion in solution by a more active metal as predicted by the electromotive series.

When considering galvanic corrosion, it is essential to know which metal will suffer accelerated corrosion. This is indicated in a rough way by the positions of metal in the"standard electromotive series." This series holds only for metals in particular concentrations (actually for unit activity) of their own salts at one atmosphere pressure.

ELECTROMOTIVE FORCE SERIES

Electrode Reaction	Standard Electrode Potential E° (volts), 25°c	Electrode Reaction	Standard Electrode Potential E° (volts), 25°c
$K = K^+ + e^-$	-2.922	$Ni = Ni^{++} + 2e^-$	-0.250
$Ca = Ca^{++} + 2e^-$	-2.87	$Sn = Sn^{++} + 2e^-$	-0.136
$Na = Na^+ + e^-$	-2.712	$Pb = Pd^{++} + 2e^-$	-0.126
$Mg = Mg^{++} + 2e^-$	-2.34	$H2 = 2H^{++} + 2e^-$	-0.000
$Be = Be^{++} + 2e^-$	-1.70	$Cu = Cu^{++} + 2e^-$	0.345
$Al = Al^{+++} + 3e^-$	-1.67	$Cu = Cu^+ + e^-$	0.522
$Mn = Mn^{++} + 2e^-$	-1.05	$2Hg = Hg2 + 2e^-$	0.799
$Zn = Zn^{++} + 2e^-$	-0.762	$Ag = Ag^+ + e^-$	0.800
$Cr = Cr^{+++} + 3e^-$	-0.71	$Pd = Pd^{++} + 2e^-$	0.83
$Ga = Ga^{+++} + 3e^-$	-0.52	$Hg = Hg^{++} + 2e^-$	0.854
$Fe = Fe^{++} + 2e^-$	-0.440	$Pt = Pt^{++} + 2e^-$	ca 1.2
$Cd = Cd^{++} + 2e^-$	-0.402	$Au = Au^{+++} + 3e^-$	1.42
$Tl = Tl^+ + e^-$	-0.336		
$Co = Co^{++} + 2e^-$	-0.277		

The gas hydrogen is used as an arbitrary reference element. Above hydrogen in the series the metals become increasingly reactive. Below hydrogen, the metals become increasingly inert. The electromotive series

also shows which metals can displace other metals in solution and thereby suffer corrosion in the process. Any metal may displace one that appears below it in this series. Thus iron can displace copper from solution with the copper ions acting as the acceptors for electrons in the corrosion of the iron. The displaced copper appears as a coating on the immersed iron surface.

(b) The demonstration of the driving force in galvanic corrosion or the potential developed in a couple of dissimilar metals.

One factor which determines the speed at which galvanic corrosion will proceed is the magnitude of difference in electric potential between the two metals. A metal coupled with another close to it in the electromotive force series will usually corrode more slowly than when coupled with one further below it. The higher the potential, the greater will be the driving force behind the galvanic corrosion. As the galvanic corrosion reaction proceeds, there is an accumulation of reaction products at the anode and at the cathode. Because of this the initial potential or driving force tends to diminish.

> "The potential of the anode drifts toward that of the cathode, and that of the cathode drifts toward that of the anode. This change in potential is called polarization; that at the anode, anodic polarization; and that at the cathode, cathodic polarization."[3]

(c) The demonstration of the influence of cathode area on the magnitude of galvanic corrosion.

In most corrosion reactions, the polarization that occurs at the cathodes exerts more of a controlling influence than the polarization at the anodes.

One cause of this may be an accumulation of hydrogen so as in effect to cover cathodic surfaces and thereby restrain corrosion at the anodes until the hydrogen is removed by one or another of the cathodic reactions, such as evolution as gas or union with oxygen to form water.

The cathodic reactions do not proceed with equal facility on all metal surfaces. As a result, some metals polarize more readily than others, and it is necessary to know something about polarization characteristics as well as initial potentials before it is possible to predict the extent of galvanic corrosion with any particular couple of metals.

This change in potential, or polarization, is a function not just of current but of current density. For the same amount of current, the current density on a small electrode will be greater than on a large electrode. With a large cathode the hydrogen that reaches it will be spread out and will be more accesible for removal by reaction with oxygen.

An example of this effect in galvanic corrosion is provided by an experiment in which pieces of steel of the same size are connected in an aerated salt solution to pieces of copper of different sizes, one small and one large. Both couples will generate current, but the couple with the large cathode produces the higher current. When the supply of oxygen is cut off and cathodic polarization is allowed to occur, it will be observed that the current drops off faster in the couple with the small cathode than it does with the large cathode. The action of oxygen as a cathodic depolarizer can be shown again by restoring the flow of oxygen and observing how the corrosion current increases once more.

(d) The demonstration that an ion concentration gradient in a

solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

The same type of cell that develops between two different metals may also develop on a single metal surface. Differences in potential from point to point can be created by differences in environment. The concentration of metal ions in the corroding solution at one point on the metal surface may become greater than at another point, with the metal in contact with the solution of greater metal ion concentration becoming the cathode and the metal in contact with the lower concentration acting as the anode and being corroded. This will cause electricity to flow between the two points.

(e) The demonstration that an oxygen concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

Oxygen concentration cells can also be set up to cause destructive corrosion. Cathodes are developed at the areas of high oxygen concentration, and anodes at the areas of low concentration where corrosion occurs. The fact that electricity does flow between points where oxygen concentrations differ may be demonstrated with similar pieces of steel in each side of a two compartment cell containing a dilute sodium chloride solution. No current flows when they are coupled through a microammeter; but if nitrogen is bubbled through one side of the cell to reduce the oxygen concentration, and oxygen through the other side to increase the oxygen content, it is

found that electricity is flowing because of the difference in oxygen concentrations.

(f) The demonstration of the corrosion resistance and nobility of iron when in the passive condition.

In higher concentration, oxygen can also retard corrosion. Oxygen, or oxidizing agents such as nitric acid, can form invisible protective films of their own and in this manner reduce corrosive action. "The metal is said to have been rendered passive."[4] When some active metals become passive, they take on many features of the noble metals. Iron made passive by an oxygen layer or oxide film approaches the noble potential of platinum and resists corrosion. When iron is coupled galvanically to platinum in a hydrochloric acid solution, the potential is about 350 millivolts. If nitric acid is used the potential difference is about 150 millivolts.

The film responsible for the passivity of the iron in the nitric acid is easily damaged. If a piece of iron with this protective coating is dipped into copper sulfate, no plating out of copper occurs but a "light tap" is sufficient to rupture the passive film. The iron strip becomes active again. Copper plates out radially form the point where the film on the iron strip is broken. An active area at the point of impact becomes anodic to the surrounding passive area acting as a cathode. The reducing action at the cathode destroys passivity and corrosive action spreads.

(g) The demonstration of the passivation of steel in oxidizing environment by alloying it with chromium or chromium and nickel.

By alloying iron with chromium or a combination of chromium and

nickel, it can be given a much more stable passivity. When the alloy contains about 12 per cent or more of chromium, it achieves substantial passivity, and will resist corrosion in many environments. The 18 per cent chromium-8 per cent nickel stainless steel is also passive in copper sulfate, as it is in nitric acid and many other oxidizing media. This passivity is substantial and cannot be destroyed by shock.

(h) The demonstration of the active and passive electrode potentials of stainless steel.

The change from passivity to activity also changes the potential of stainless steel. This can be shown by immersing a piece of 18-8 stainless steel and a piece of carbon steel in warm sulfuric acid and joined through a millivoltmeter to measure their difference in potential. At the start the stainless steel is passive and shows a potential of 550 millivolts. The carbon steel is then brought into direct contact with the stainless steel under the solution. Hydrogen now forms on the stainless steel surface and destroys the film responsible for its passivity and its noble potential. When the piece of carbon steel is taken away, it is found that the potential difference between the stainless steel and the carbon steel has fallen towards zero. When another piece of stainless steel which is still passive is introduced, it is found that the potential difference between this passive stainless steel and the active stainless is as great as that observed between ordinary steel and the passive stainless steel. The passivity of the activated stainless steel by introducing nitric acid which has a strong passivating effect. The evolution of hydrogen on the activated stainless steel stops, and the potential drops toward zero.

APPARATUS AND MATERIALS

The materials and apparatus used in the experiments demonstrating corrosion of metals in aqueous solutions were:

(a) The illustration of the displacement of an ion in solution by a more active metal as predicted by the Electromotive Series.

Four 400 ml. beakers
Copper sulfate, 5% solution (250 ml.)
Hydrochloric acid, 10% solution (250 ml.)
Silver nitrate, 5% solution (250 ml.)
One strip of iron or carbon steel (1" x 5" x 1/16")
One strip of zinc (5¼" x ½" x ¼")
One strip of copper (1" x 5" x 1/16")
Distilled water

(b) The demonstration of the driving force in galvanic corrosion or the potential developed in a couple of dissimilar metals.

3% sodium chloride solution (1000 ml.)
One strip of zinc (5¼" x ½" x ¼")
One strip of sheet aluminum (1" x 6" x 1/32")
One strip of sheet copper (1" x 6" x 1/16")
One 1000 ml. beaker
One millivoltmeter, 0-1000 mv. D. C.
Wire leads and clips

(c) The demonstration of the influence of cathode area on the magnitude of galvanic corrosion.

Two 800 ml. beakers
Two strips of carbon steel (5¼" x 2" x 1/16")
One piece of sheet copper (3-1/16" x 3/4" x 1/32")
One piece of sheet copper (5" x 7" x 1/16")
Two milliammeters (0-100 ma.)
Wire for connecting milliammeters to metal strips
Sodium chloride solution -3%- (1600 ml.)
Oxygen
Glass tubing (Used as a gas bubbler)
Rubber tubing (to connect bubbler to oxygen)

APPARATUS AND MATERIALS (cont'd)

(d) The demonstration that an ion concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations. (4)

Two 600 ml. beakers
600 ml. 0.001% copper sulfate solution
600 ml. 10% copper sulfate solution
Concentrated sulfuric acid
Two strips of copper (2" x 6" x 1/16")
One U-tube for a salt bridge
Agar agar
One microammeter (0-1000 microamperes)
One millivoltmeter (0-200 mv.)
Wire and clips for connecting strips to meters

(e) The demonstration that an oxygen concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations. (5)

Two 600 ml. beakers
1200 ml. -3%- sodium chloride solution (deaerated by boiling)
Two strips of low carbon steel (4-7/8" x 2-1/16" x 1/16")
One U-tube for a salt bridge
Agar Agar
One microammeter (0-200 microamperes)
Wire and clamps for connection

(f) The demonstration of the corrosion resistance and nobility of iron when in the passive condition. (6)

One D. C. millivoltmeter (0-1000 mv.)
One strip iron (6¼" x 2" x 1/16")
One strip iron (3" x 2" x 1/16")
One strip platinum (1" x 2" x 1/32")
Hydrochlorec acid - 6 normal
Nitric acid concentrated
Distilled water

APPARATUS AND MATERIALS (cont'd)

Copper sulfate solution -10%-(1000 ml.)
Wires and clips
Two glass rods
Three 1000 ml. beakers

(g) The demonstration of the passivation of steel in oxidizing environments by alloying it with chromium or chromium and nickel.

One piece of carbon steel (2" x 6" x 1/16")
One piece of (405) chromium steel (2" x 8" x 1/16")
One piece of (430) chromium steel (9" x 2" x .025")
One piece of (304) chromium steel (8" x 3/8" x .020")
One piece of (309) chromium steel (8" x 3/8" x .020")
One piece of (310) chromium steel (8" x 3/8" x .020")
One piece of Inconel (2" x 8" x 1/16")

(h) The demonstration of the active and passive electrode potentials of stainless steel.

Two strips 18-8 chromium-nickel stainless steel ($1\frac{1}{2}$" x 6" x 1/16")
One strip carbon steel ($1\frac{1}{2}$" x 6" x 1/16")
Sulfuric acid - concentrated
Nitric acid - concentrated
Distilled water
Millivoltmeter 0-1000 mv. D. C.
Wires and clips
One 1000 ml. beaker
One 250 ml. beaker

COMPOSITION PERCENT OF STAINLESS STEEL

	CARBON	CHROMIUM	NICKEL	OTHER ELEMENTS
304	0.08 max.	18.0 to 20.0	8.0 to 11.0	Mn. max. 2
309	0.20 max.	22.0 to 24.0	12.0 to 15.0	Mn. max. 2
310	0.25 max.	24.0 to 26.0	19.0 to 22.0	Mn. max. 2
405	0.08 max.	11.5 to 13.5	----------	Al. 0.1 to 0.3
430	0.12 max.	14.0 to 18.0	----------	----------

Inconel (5)

Nomial Comp.	15%	80	5%

EQUIPMENT



Figure 2 Equipment used in experiment (a) showing the displacement of copper by iron in a copper sulfate solution.



Figure 3 Equipment used in experiment (a) showing the displacement of hydrogen from hydrochloric acid by zinc.

EQUIPMENT (cont'd)



Figure 4 Equipment used in experiment (a) showing the displacement of silver by copper in a silver nitrate solution.

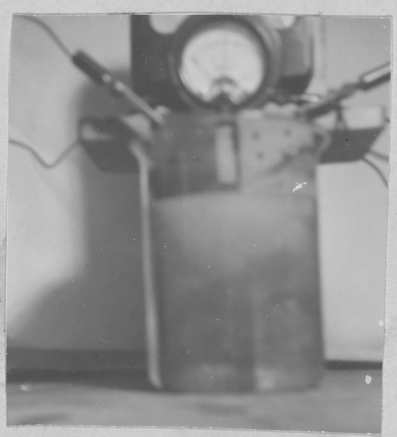


Figure 5 Equipment used in experiment (b) showing the potential developed between dissimilar metals in a galvanic couple.

EQUIPMENT (cont'd)

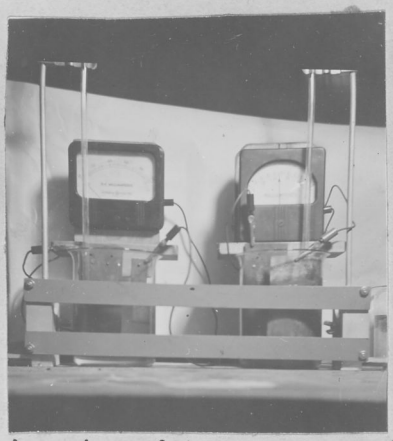


Figure 6 Equipment used in experiment (c) showing the influence of cathode area on corrosion illustrated by steel-copper couples in sodium chloride solution.



Figure 7 Equipment used in experiment (d) demonstration that ion concentrations gradients in a solution covering a metal surface can generate corrosion currents.

EQUIPMENT (cont'd)

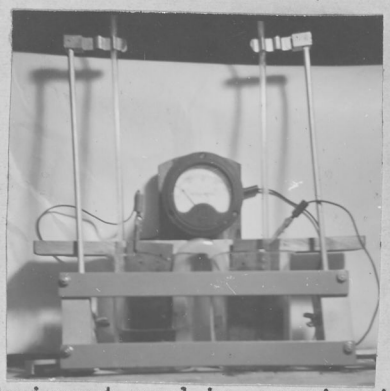


Figure 8 Equipment used in experiment (e) demonstration that an oxygen concentration gradient in a solution covering a metal surface can generate corrosion current.



Figure 9 Equipment used in experiment (f) demonstration of the corrosion resistance and nobility of iron when in the passive condition.

EQUIPMENT (cont'd)

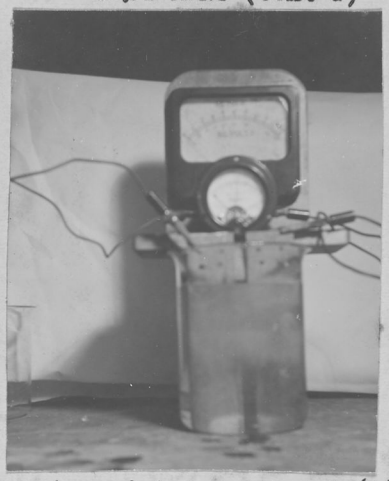


Figure 10 Equipment used in experiment (h) demonstration of the active and passive electrode potentials of stainless steel.

PROCEDURE

(a) The illustration of the displacement of an ion in solutions by a more active metal as predicted by the Electromotive Series.

(1) A strip of carbon steel was immersed in 5% copper sulfate solution.

(2) A strip of zinc was immersed in 10% hydrochloric acid.

(3) A strip of copper was immersed in 10% hydrochloric acid.

(4) A strip of copper was immersed in 5% silver nitrate solution.

(b) The demonstration of the driving force in galvanic corrosion or the potential developed in a couple of dissimilar metals.

(1) Strips of zinc and aluminum were suspended in a beaker of 3% soldium chloride solution. The strips were then connected to a millivoltmeter.

(2) Strips of zinc and copper were suspended in a beaker of 3% sodium chloride solution. The strips were then connected to a millivoltmeter.

(c) The demonstration of the influence of cathode area on the magnitude of galvanic corrosion.

(1) Strips of steel and copper were suspended in a 3% sodium chloride solution and oxygen was bubbled through the solution. The steel strip was connected to the negative terminal and copper to the positive terminal of a milliammeter.

(2) Same as (1) except the size of the copper strip is changed. The large strip of copper was used.

(3) The flow of oxygen was stopped in both beakers.

(4) The oxygen flow was restored.

PROCEDURE (cont'd)

(d) The demonstration that an ion concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

(1) A salt bridge was made by boiling 1.5 grams of agar agar in 50 ml. of 10% copper sulfate solution and then this mixture was poured into a U-tube to set and gel.

(2) A strip of copper was suspended in each of two beakers; one beaker containing 0.001% copper sulfate and the other contained 10% copper sulfate solution. Each was acidified to 10% acid by adding concentrated sulfuric acid. First they were connected by using the salt bridge made in (1). The metal strips were then connected to a microvoltmeter.

(3) Same as (2) except 1% copper sulfate solution was used instead of 10%.

(4) Same as (2) except different concentrations are used instead of 10% copper sulfate solution. The solutions used were 0.1%, 0.01%, and 0.001% copper sulfate solutions.

(e) The demonstration that an oxygen concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

(1) A salt bridge was made by dispersing 1.5 agar agar in 50 ml. 3% soldium chloride solution.

(2) Two beakers were filled with 3% sodium chloride solution and the solutions were then connected with salt bridge made in (1). A strip of steel was suspended in each beaker and connected to a micro-amperes. One strip was moved until the current is zero. Then oxygen was bubbled in one solution and nitrogen was bubbled through the other.

PROCEDURE (cont'd)

(f) The demonstration of the corrosion resistance and nobility of iron when in the passive condition.

(1) Strips of iron and platinum were suspended in hydrochloric acid. The strips were then connected to a millivoltmeter.

(2) Same as (1) except nitric acid was used instead of hydrochloric acid.

(3) A strip of iron was suspended in nitric acid, rinsed in distilled water, and then immersed in 10% copper sulfate solution. Then the strip of iron was tapped with a glass rod.

(g) The demonstration of the passivation of steel in oxidizing environments by alloying it with chromium or chromium and nickel.

(1) Strips of different metals were immersed in 10% copper sulfate solution. The strips that were used:

Carbon steel
304 stainless steel
309 stainless steel
310 stainless steel
405 stainless steel
430 stainless steel
Inconel steel

(2) The 405 stainless steel was reimmersed in the copper sulfate solution. It was then removed and tapped with a glass rod.

(3) Same as (2) except 304 stainless steel was used.

(h) The demonstration of the active and passive electrode potentials of stainless steel.

(1) A strip of carbon steel and a strip of 18-8 stainless steel were suspended in a solution of sulfuric acid and distilled water. They were then connected to a millivoltmeter.

PROCEDURE (cont'd)

(2) The carbon steel was brought into contact with the stainless steel under the surface of the acid. The carbon steel was then separated from the stainless steel strips.

(3) The carbon steel was replaced with another strip of stainless steel.

(4) Nitric acid was added to sulfuric acid solution.

RESULTS

(a) The illustration of the displacement of an ion in solution by a more active metal as predicted by the Electromotive Series.

(1) After 5 minutes the strip of carbon steel that was immersed in 5% copper sulfate solution was coated with copper. Only the part that was immersed was coated.

(2) There was a vigorous evolution of hydrogen as the zinc that was immersed in the 10% hydrochloric acid corroded and displaced hydrogen from the solution. The zinc surface was also etched.

(3) There was no noticeable reaction when copper was placed in 10% hydrochloric acid.

(4) There was a deposition of silver on the strip of copper which was placed in 5% silver nitrate solution.

(5) The time required to perform the experiments was fifteen minutes.

(b) The demonstration of the driving force in galvanic corrosion or the potential developed in a couple of dissimilar metals.

(1) The potential developed between zinc and aluminum in 3% sodium chloride solution was:

VOLTS	TIME (min.)	VOLTS	TIME (min.)
0.35	1	0.35	11
0.35	2	0.35	12
0.35	3	0.35	13
0.35	4	0.35	14
0.35	5	0.35	15
0.35	6	0.35	16
0.35	7	0.35	17
0.35	8	0.35	18
0.35	9	0.35	19
0.35	10	0.35	20

RESULTS (cont'd)

(2) The potential developed between zinc and copper in 3% sodium chloride solution was:

VOLTS	TIME (min.)	VOLTS	TIME (min.)
0.92	1	0.72	11
0.88	2	0.71	12
0.86	3	0.69	13
0.84	4	0.68	14
0.82	5	0.68	15
0.80	6	0.67	16
0.79	7	0.65	17
0.78	8	0.65	18
0.75	9	0.63	19
0.73	10	0.63	20

(3) The time required to perform the experiment was sixty minutes.

(c) The demonstration of the influence of cathode area on the magnitude of galvanic corrosion.

(1) The current developed between a strip of steel and a small piece of copper which were suspended in a 3% sodium chloride solution saturated with oxygen was:

CURRENT	TIME (min.)	CURRENT	TIME (min.)
9 millamps.	1	8.5 millamps.	8
7.5	2	8.5	9
8.0	3	8.5	10
8.5	4	9.0	11
8.0	5		
8.5	6		
8.5	7		

(2) The current developed between a strip of steel and a large piece of copper which were suspended in a 3% sodium chloride solution saturated with oxygen was:

CURRENT	TIME (min.)	CURRENT	TIME (min.)
63 millamps.	0	51.5 millamps.	6
53.0	1	51.0	7
52.0	2	50.5	8
52.5	3	50.5	9
52.0	4	50.0	10
52.0	5		

RESULTS (cont'd)

(3) The current developed in (1) and (2) when the oxygen supply was cut off was:

(1)

CURRENT	TIME (min.)
7.00 millamps.	0.0
4.50	0.5
3.75	1.0
3.50	1.5
3.25	2.0
3.00	2.5
3.00	3.0
3.00	3.5
3.00	4.0
3.00	4.5
3.00	5.0
3.00	5.5
3.00	6.0
3.00	6.5
3.00	7.0
3.00	7.5
3.00	8.0
3.00	8.5
3.00	9.0
3.00	9.5
3.00	10.0

(2)

CURRENT	TIME (min.)
48.0 millamps	0.0
34.0	0.5
30.5	1.0
29.0	1.5
27.0	2.0
25.5	2.5
24.0	3.0
23.0	3.5
22.0	4.0
21.5	4.5
20.0	5.0
20.0	5.5
19.5	6.0
19.0	6.5
18.5	7.0
18.0	7.5
18.0	8.0
17.75	8.5
17.75	9.0
17.50	9.5
17.50	10.0

(4) The current developed in (1) and (2) when the oxygen supply was restored was:

(1)

CURRENT	TIME (min.)
2.5 millamps.	0.0
9.0	0.5
9.0	1.0
9.0	1.5
9.0	2.0
9.5	2.5
9.5	3.0
9.0	3.5
9.5	4.0
9.5	4.5
9.5	5.0
9.5	5.5

(2)

CURRENT	TIME (min.)
16 millamps.	0.0
46	0.5
45	1.0
45	1.5
45	2.0
46	2.5
46	3.0
46	3.5
46	4.0
45	4.5
46	5.0
46	5.5

RESULTS (cont'd)

(c) cont'd

(5) The time required to perform the experiment was sixty minutes.

(d) The demonstration that an ion concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

(1) A salt bridge was made.

(2) The potential and current developed between a strip of copper in 10% copper sulfate solution and a strip of copper of the same size in a solution of 0.001% copper sulfate solution was:

CURRENT	VOLT
150 microamps.	0.03 Mils.

The copper in the 10% was the cathode.
The copper in the 0.001% was the anode and suffer corrosion.

(3) The potential and current developed between a strip of copper in 1% copper sulfate solution and a strip of copper of the same size in a solution of 0.001% copper sulfate solution was:

CURRENT	VOLT
37.5 micamps	0.03 Mils.

Copper strip in 1% solution was the cathode.

(4) Same as (3) except different concentrations are used instead of 10% copper sulfate solution.

	CURRENT	VOLT
0.1%	7.5 microamp	0.01
0.01%	1.0	0.005
0.001%	0.5	0.0025

The copper strips in the higher concentrations were the cathodes.

(5) The time required for the experiment was twenty minutes.

RESULTS (cont'd)

(e) The demonstration that an oxygen concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

(1) A salt bridge was made as described in the procedure.

(2) The current developed between a strip of steel in a 3% sodium chloride solution in which oxygen had been bubbled and a strip of steel of the same size in a 3% sodium chloride solution in which nitrogen had been bubbled was:

CURRENT
145 microamperes

Steel in the high oxygen concentration was the cathode and the steel in the low oxygen concentration was the anode and suffered corrosion.

(3) The time required for the experiment was twenty minutes.

(f) The demonstration of the corrosion resistance and nobility of iron when in the passive condition.

(1) The potential developed between a strip of iron and platinum suspended in hydrochloric acid was:

VOLTS
0.90 volts

(2) The potential developed between strips of iron and platinum suspended in nitric acid was:

VOLTS
0.45 volts

(3) Copper did not plated out on the piece of iron which was suspended in nitric acid, rinsed in distilled water and then immersed in 10% copper sulfate solution. When this piece of iron was then tapped with a glass rod, copper began to plate out at the point where the passive film was broken and spreaded from this point over the entire surface.

RESULTS (cont'd)

(f) cont'd

(4) The time required for the experiment was twenty minutes.

(g) The demonstration of the passivation of steel in oxidizing environments by alloying it with chromium or chromium and nickel.

(1) Different metals were immersed in 10% copper sulfate solution. The results were:

Carbon steel - Copper plated out on the surface that was immersed.

304 Stainless Steel - Copper did not plate out.

309 Stainless Steel - Copper did not plate out.

310 Stainless Steel - Copper did not plate out.

405 Stainless Steel - Copper did not plate out.

430 Stainless Steel - Copper did not plate out.

Inconel - Copper did not plate out.

(2) The 405 Stainless steel was reimmersed in the copper sulfate solution. It was removed and tapped with a glass rod.

Results

The strongly passive condition resulting from the presence of 12% chromium was not destroyed by mechanical shock.

(3) Same as (2) except 304 stainless steel was used. The results were the same as (2).

(4) The time required for the experiment was fifteen minutes.

RESULTS (cont'd)

(h) The demonstration of the active and passive electrode potentials of stainless steel.

(1) The potential developed between a strip of carbon steel and a strip of 18-8 stainless steel suspended in sulfuric acid was:

VOLTS
0.55 volts
carbon steel was active and suffered corrosion
18-8 stainless steel was not active

(2) The potential developed when the strip of carbon steel was brought into contact with the stainless steel under the surface of the solution was:

VOLTS
0.15 volts
Hydrogen evoluted from both strips. Both strips were now active.

(3) The potential developed between a strip of 18-8 stainless steel and the active stainless steel in (2) was:

VOLTS
0.55 volts
The new strip was passive but the active strip still generated current.

(4) The potential of (3) when nitric acid was added to the sulfuric acid was:

VOLTS
0.15 volts
Evolution of hydrogen ceased on the active specimen. The nitric acid caused the strip to become passive again.

(5) The time required for the experiment was fifteen minutes.

Discussion of Results

The results obtained were in close agreement with those reported in the report "Corrosion in Action." The greatest deviation came in experiment (d) which was concerned with corrosion due to ion concentration differences. In the report the current flow was reported to be about 400 microamperes and a potential of 50 millivolts. In the present experiment the current flow was found to be only 150 microamperes and the potential to be only .16 millivolt. The error was probably due to the fact that the salt bridge did not make a good connection between the solution. In experiment (g) which was concerned with the passivation of steel by alloying it with chromium the picture was not completely shown because 3% and 6% chromium were not available. The percentages which were used showed that chromium steel did not suffer corrosion.

Conclusion and Recommendations

The experiments showed clear and definite results, and they could be performed in a reasonably short time. Therefore, it is recommended that these experiments be set up as laboratory exercises. The experiments demonstrated certain fundamental concepts in the aqueous corrosion of metals and alloys.

It is suggested that higher concentrations of copper sulfate solution be used in experiment (d) in order to obtain clearer results. It is also suggested that 3% and 6% chromium steel be obtained for experiment (g). This would show the corrosive action upon steel with less than 12% chromium.

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned does not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

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Title Associate Professor

Date 3/19/57

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APPENDIX

Original Data

Date: Jan. 31, 1957

Corrosion in Aqueous Solutions Ch. E. 401

Purpose: To illustrate the displacement of an ion in solution by a more active metal as predicted by the Electromotive Series.

(a) A strip of carbon steel was immersed in 5% copper sulfate solution.

Results: After 5 minutes the part of the strip that had been immersed was coated with copper.

(b) A strip of zinc was immersed in 10% hydrochloric acid.

Results: There was a vigorous evolution of hydrogen as the zinc corroded and displaced it from the solution. The zinc surface was also etched.

(c) A strip of copper was immersed in 10% hydrochloric acid.

Results: There was no noticeable reaction.

(d) A strip of copper was immersed in 5% silver solution.

Results: After 2 minutes there was 1.2 grams of silver deposited on the strip of copper.

Area of copper strip immersed was 5 square inches.

(e) Time to conduct the experiment was fifteen minutes.

Original Data

Date: Feb. 1, 1957

Corrosion in Aqueous Solutions Ch. E. 401

Purpose: To demonstrate the driving force in galvanic corrosion or the potential developed between dissimilar metals in a galvanic couple.

(a) Strips of zinc and aluminum were suspended in a beaker of 3% chloride solution. The strips were then connected to a millivolt meter.

Results:

Volts	Time (min.)	Volts	Time (min.)
0.35	1	0.35	11
0.35	2	0.35	12
0.35	3	0.35	13
0.35	4	0.35	14
0.35	5	0.35	15
0.35	6	0.35	16
0.35	7	0.35	17
0.35	8	0.35	18
0.35	9	0.35	19
0.35	10	0.35	20

Zinc ($5\frac{1}{4}$ x $\frac{1}{4}$ x 3/32) was the anode- Aluminum (1 x 6 x 1/32) was the cathode.

(b) Strips of zinc and copper were suspended in a beaker of 3% sodium chloride solution. The strips were then connected to a millivolt meter.

Results:

Volts	Time (min.)	Volts	Time (min.)
0.92	1	0.72	11
0.88	2	0.71	12
0.86	3	0.69	13
0.84	4	0.68	14
0.82	5	0.68	15
0.80	6	0.67	16
0.79	7	0.65	17
0.78	8	0.65	18
0.75	9	0.63	19
0.73	10	0.63	20

Strips: zinc ($5\frac{1}{4}$ x $\frac{1}{4}$ x 3/32) anode -- Copper (7/8 x 6 x 1/16) cathode

(c) Time for the experiment was sixty minutes.

Original Data

Date: Feb. 2, 1957

Corrosion in Aqueous Solutions Ch. E. 401

Purpose: To demonstrate the influence of area of the cathode material on the magnitude of galvanic corrosion.

(a) Strips of steel and copper were suspended in a 3% sodium chloride solution and oxygen was bubbled through the solution. The steel strip was connected to negative pole and copper to the positive terminal of a milliammeter.

Copper Steel

Current	Time (min.)	Current	Time (min.)
9 millamps.	0	8.5 millamps.	7
7.5	1		8
8.0	2		9
8.5	3		10
8.0	4		
8.5	5		
8.5	6		

Area: Steel ($5\frac{1}{4}$x2x1/16) Area under solution: (3-1/8x2x1/16)
Copper (3-1/16x3/4x1/32) ($1\frac{1}{2}$x3/4x1/32)

(b) Same as above except the size of the copper is: (5x7x1/16)
Under solution the area was (3-5/8x7x1/16)

Current	Time (min.)	Current	Time (min.)
63 millamps.	0	51.5 millamps.	
53	1	51	
52	2	50.5	
52.5	3	50.5	
52	4	50	
52	5		

(c) Now the flow of oxygen is stopped in experiments (a) and (b).

Original Data

Date: Feb. 2, 1957

Corrosion in Aqueous Solutions Ch. E. 401

(c) Cont'd

Large Copper Strip

Current	Time (min.)
48 millamps.	0
34	.5
30.5	1
29.0	1.5
27.0	2
25.5	2.5
24.0	3
23.0	3.5
22.0	4
21.5	4.5
20.0	5
20.0	5.5
19.5	6
19.0	6.5
18.5	7
18.0	7.5
18.0	8
17.75	8.5
17.75	9
17.50	9.5
17.50	10

Small Copper Strip

Current	Time (min.)
7 millamps.	0
4.5	.5
3.75	1
3.50	1.5
3.25	2
3.00	2.5
3.00	3
3.00	3.5
3.00	4
3.00	4.5
3.00	5
3.00	5.5
3.00	6
3.00	6.5
3.00	7
3.00	7.5
3.00	8
3.00	8.5
3.00	9
3.00	9.5
3.00	10

(d) The oxygen flow was then restored:

Large Copper Strip

Current	Time (min.)
16 millamps.	0
46	.5
45	1
45	1.5
45	2
46	2.5
46	3
46	3.5
46	4
46	4.5
46	5

Small Copper Strip

Current	Time (min.)
2.5 millamps.	0
9	.5
9	1
9	1.5
9.5	2
9.5	2.5
9.0	3
9.5	3.5
9.5	4
9.5	4.5
9.5	5

(e) Time required for the experiment was sixty minutes.

Original Data

Date: Feb. 5, 1957

Corrosion in Aqueous Solution Ch. E. 401

Purpose: To demonstrate that ion concentration gradients in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

(a) A salt bridge was made by boiling 1.5 gms. agar agar in 50 ml. of 10% copper sulfate solution and then this mixture was poured into a U-tube to set as a gel.

(b) A strip of copper was suspended in each of two beakers; one beaker containing .001% copper sulfate and the other contained 10% copper sulfate solution. Each was acidified to 10% acid by adding conc. sulfuric acid. First they were connected by using the salt bridge made in (a). The metal strips were connected then to a microammeter and then to a millivoltmeter.

Results:	Current	Voltage
	150 microamps	.16 mils

The copper in the 10% solution was the cathode.
The copper in the .001% solution was the anode.

(c) Same as (b) except 1% copper sulfate solution was used instead of 10%.

Results:	Current	Voltage
	37.5 microamps	.03 mils

Copper strip in 1% solution was the cathode.

(d) Same as (b) except different concentrations are used instead of 10% copper sulfate solution. .1%, 101%, and .001% were used

	Current	Voltage
.1%	7.5 microamps	.01 mils
.01%	11.0	.005
.001%	.05	.0025

(e) Time required for experiment was twenty minutes.

Original Data

Date: Feb. 7, 1957

Corrosion in Aqueous Solutions

Purpose: To demonstrate the corrosion resistance and nobility of iron when in the passive condition.

(a) Strips of iron and platinum were suspended in hydrochloric acid. The strips were then connected to a millivoltmeter.

Results:

Volts	Strips
.9 volts	Pt. (1x2x1/32)
	Fe. ($6\frac{1}{4}$x2x1/16)

(b) Same as (a) except nitric acid is used instead of hydrochloric.

Results:

Volts
.425

(c) A strip of iron was suspended in nitric acid, rinsed in distilled water, and then immersed in 10% copper sulfate solution.

Results: Copper did not plate out on the iron.

Then the suspended iron is tapped with a glass rod.

Results: There was a deposition of copper as the passive film is ruptured by the mechanical shock.

Iron (1/16x2x3)

(d) Time for the experiment was twenty minutes.

Original Data

Date: Feb. 7, 1957

Corrosion in Aqueous Solutions Ch. E. 401

Purpose: To demonstrate the active and passive electrode potentials of stainless steel.

(a) A strip of carbon steel and a strip of 18-8 stainless steel were suspended in a solution of sulfuric acid and distilled water. They were then connected to a millivoltmeter.

Results:

Volts	
.55 volt	carbon steel is active 18-8 stainless steel is not active

(b) The carbon steel was brought into contact with the stainless steel under the surface of the acid.

Results:

Volts	
.15 volt	Hydrogen evolution comes from both strips Both strips are now active.

(c) The carbon steel was replaced with another strip of 18-8 stainless steel.

Results:

Volts	
.55 volt	The new strip was passive but the active strip still generates current.

(d) Nitric acid was added to sulfuric acid solution.

Results:

Volts	
.15 volt	Evolution of hydrogen ceases on active specimen. Nitric acid causes the strip to become passive again.

(e) Time required for the experiment was fifteen minutes.

Original Data

Date: Feb. 7, 1957

Corrosion in Aqueous Solutions Ch. E. 401

Purpose: To demonstrate that an oxygen concentration gradient in a solution covering a metal surface can generate corrosion currents between the metal areas in contact with the solution of different concentrations.

(a) A salt bridge was made by dispersing 1.5 agars- agar in 50 ml. 3% sodium chloride solution.

(b) Two beakers were filled with 3% sodium chloride solution and the solution were then connected with the salt bridge. A strip of steel was suspended in each beaker and connected to a microamperes. One strip was moved until the current is zero. Then oxygen was bubbled in one solution and nitrogen was bubbled through the other.

Results: After 2 min. Current
145 microamps
Steel in high oxygen conc. is cathode
Steel in low oxygen conc. is anode and suffers corrosion.

(c) Time required for experiment was 20 minutes.

Original Data

Date: Feb. 14, 1957

Corrosion in Aqueous Solutions Ch. E. 401

(a) Strips of different metals were immersed in 10% copper sulfate solution.

Results:

Carbon steel	----------Copper plated out.
304 Stainless Steel	----------Copper did not plate out.
309 Stainless Steel	----------Copper did not plate out.
310 Stainless Steel	----------Copper did not plate out.
405 Stainless Steel	----------Copper did not plate out.
430 Stainless Steel	----------Copper did not plate out.
Inconel	----------Copper did not plate out.

(b) The 12% chromium steel was reimmersed in the copper sulfate solution. It was removed and tapped with a glass rod.

Results: The strongly passive condition resulting from the presence of 12% chromium was not destroyed by mechanical shock.

(c) Same as (b) except 304 stainless steel is used.

Results: Same as in (b)

	COMPOSITION %			
	Carbon	Chromium	Nickel	Other elements
309	.20 max.	22.0 to 24.0	12 to 15	Mn. max. 2
310	.25 max.	24.0 to 26.0	19 to 22	Mn. max. 2
405	.08 max.	11.5 to 13.5	--------	Al. .1 to .3
430	.12 max.	14.0 to 18.0	--------	----------
(nomial)				
Inconel		15	80	5%
304	.08 max.	18.0 to 20.0	8 to 11	Mn. max. 2