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INVESTIGATION OF CORROSION POTENTIALS
OF ALUMINUM-COPPER GALVANIC COUPLES

by

Harry L. Brown

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science.

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INTRODUCTION

The Galvanic Cell

In the year 1791 the Italian scientist Galvani performed his famous experiment with two unlike metals and the legs of a frog. From his name is derived the word "galvanic," referring to the phenomenon of an electric current from the wet contact of two dissimilar metals.

The Italian physicist, Volta, correctly analyzed the work of Galvani, and in 1792 published his findings on couples of unlike metals. His list, the forerunner of the modern "e.m.f. series" of metals, included zinc, tin, lead, iron, brass, copper, bronze, platinum, gold, silver, mercury, and graphite.

The galvanic cell, an outgrowth of Volta's experiments, is now in everyday use as any one of a variety of the primary and secondary cells which are so necessary to home and industry.

Because it is so easily formed, the galvanic cell may also have some undesirable effects. Its mechanism involves a chemical change in one of the constituent metals. Essentially, this process is corrosion, and its cost in time and materials in one year is enormous.

The Nature of Corrosion

Generally speaking, two types of corrosion must be considered. These are chemical and electrochemical corrosion. A closer examination shows, however, that corrosion of a purely chemical nature, such as the direct oxidation of pure

iron by dry oxygen or chlorine gas, is a comparatively rare occurrence. In practice, therefore, one is concerned only with electrochemical corrosion.

Watts⁽¹⁾ classifies electrochemical corrosion in four groups, as follows:

1. Corrosion without displacement of any substance from the corroding solution.
2. Displacement of a metal from the corroding solution.
3. Corrosion with visible evolution of hydrogen.
4. Corrosion accompanied by invisible displacement of hydrogen, which is then removed physically or chemically.

The chemical changes which take place in these groups involve a transfer or flow of electrons. By Faraday's Law, the amount of current flow is proportional to the weight of metal which dissolves.

The Electrochemical Theory of Corrosion

The electrochemical theory of corrosion as advanced by Whitney and Cushman is based on the Nernst electrolytic solution pressure theory, which assumes a definite tendency toward the passage of any metal from the atomic to the ionic state, and osmotic pressure of the ions resisting this tendency. Nernst assumed that the gas laws are valid for ions of strong electrolytes, so that for a thermodynamically reversible reaction

$$e = - \frac{RT}{nF} \ln \frac{P}{k} + \frac{RT}{nF} \ln C$$

Where

e is the single-electrode potential,

R is the gas constant,

T is the absolute temperature,

P is the electrolytic solution pressure of the metal,

C is the concentration in gram ions per liter of the metal ions,

k is a constant,

n is the number of equivalents involved,

F is Faraday's constant.

The term - $\frac{RT}{nF} \ln \frac{P}{k}$ is a constant at any temperature, so that for any given concentration and temperature the single-electrode potential may be defined as the potential difference between the electrode and a normal solution of the ion in equilibrium.

Whitney and Cushman assumed that if two metals of different electrolytic solution pressures were brought into contact with one another, the metal of higher electrolytic solution pressure would dissolve, and hydrogen would be deposited on the other metal. The presence of oxygen in the water would remove the hydrogen, and corrosion could continue indefinitely. This theory has been at least partially confirmed by quantitative measurements of corrosion rates in terms of evolved hydrogen⁽²⁾.

The scope of the theory has been enlarged to include the possibility of having both anodic and cathodic areas on a single specimen. Experimental work done at Columbia University by Dr. Colin Fink⁽²⁾ indicates that the surface of any metal or alloy is composed of numerous local couples. These couples may be set up by such mechanisms as strain-hardening, inhomogeneity of the metal, difference in ex-

posure to light, difference in orientation of individual crystals, and the presence of foreign materials of all sorts. Fink observes that the strain area is usually anodic, and so tends to oxidize. Non-uniformity of the electrolyte in regard to concentration or oxygen content may also be responsible for local galvanic couples.

Nernst's theory states that dissolving of metals by corrosive media is accomplished by metal ions leaving the surface and is accompanied by a flow of current. This theory is generally accepted. Such a theory, however, implies the co-existence of cathodic areas where other ions, such as hydrogen, may be discharged. The current may be considered as flowing from anode to cathode in the external circuit.

Types of Potentials

The tendency of a metal to corrode when it is part of a galvanic cell may be expressed in terms of an oxidation or anode potential, and a reduction or cathode potential. The cell e.m.f. is equal to the difference of these two potentials. A single-electrode potential as such has little significance in galvanic corrosion, since the corrosion rate is proportional to the e.m.f. of the cell. Two types of cell potentials must be considered.

The open-circuit potential indicates a potential with no current flowing. This is an ideal situation, since in making the measurement with a potentiometer, very small currents will flow until a balance is obtained. It is possible that currents so small as to have no effect on the galvanometer circuit might be flowing even when the circuit is

apparently in balance.

Polarized potentials are those which are obtained with appreciable currents flowing in the circuit. Their values are smaller than open-circuit potentials as a result of the back e.m.f. set up by the effects of current flow.

Polarization may be chemical, caused by a chemical change on the surface of the electrodes, or it may be concentration polarization, a lack of homogeneity in the electrolyte. Concentration polarization can usually be reduced by agitating the electrolyte, whereas chemical polarization is not ordinarily so affected.

Statement of Thesis

If it is assumed that all current flowing in a galvanic cell flows through a circuit external to the solution, Ohm's law should apply to the external circuit and the potential across it will be proportional to the current. Faraday's law gives the relationship between quantity of current and electrochemical equivalents of substances reacting at the electrodes. By combining the two, a measured potential should be a qualitative indication of the corrosion rate at any given instant.

A study of Nernst's equation shows that the potential of any metal is a function both of its solution pressure and of the concentration of its ions. If none of the metal ions are present in the electrolyte before the metal electrode is immersed, it may be expected that the potential for that metal will become nearly constant at a different value than would be the case if the metal were in equilibrium with its

ions.

The purpose of this research is to measure the potentials of certain couples of aluminum-base and copper-base alloys. The use of tap water and distilled water is based on the high resistivities of these materials and their low corrosiveness as compared with solutions of acids, bases, and salts. Tap water, in particular, is often the electrolyte in cases where corrosion is the result of a galvanic couple. By these measurements a qualitative indication of corrosion rates of the various materials may be obtained.

Open-circuit cell potentials, measured by means of a potentiometer, will be taken in order to determine the possibility of duplicating corrosion potentials obtained by previous investigators. Any such check will probably involve comparing a cell potential with the sum of two single-electrode potentials.

Another line of investigation will attempt to work with potentials of short-circuited couples such as actually exist when galvanic corrosion takes place. A voltmeter of suitable range will be connected to the couple in such a manner as to allow a reading to be taken as soon as the circuit is broken. The couple will be short-circuited at all times except when a reading is being made.

EQUIPMENT

Potentiometer Circuit

The instrument used was a Leeds and Northrup, type K, portable potentiometer, with self-contained standard cell, working cell, resistances, and galvanometer. Its range is from zero to 1.11 volts. Figure 1 shows a typical circuit diagram.

When a steady state has been attained, the readings from this instrument represent only the tendency of the electrode to enter solution, and are not affected by the cell changes which take place when appreciable currents flow in the circuit.

Voltmeter Circuit

A Westinghouse, type PX-5, millivoltmeter was connected in a separate circuit. Its range is zero to 50 millivolts, and its internal resistance is 4.2 ohms. By Ohm's law this instrument draws 1.19 milliamperes of current at full scale. Its accuracy is given as one half of one percent of full scale in the range 15 deg to 30 deg C. Figure 2 shows a typical circuit diagram.

The installation of a microammeter in a separate circuit indicated that insufficient currents were generated to actuate the voltmeter accurately. As a result of this fact, the voltmeter readings must be considered to be in error, but they serve as a basis for comparing open-circuit and polarized potentials.

As indicated by the circuit diagram, a double-throw switch is used. In one position of the switch the couple is short-circuited. In the other position the short circuit is broken and the voltmeter circuit is connected.

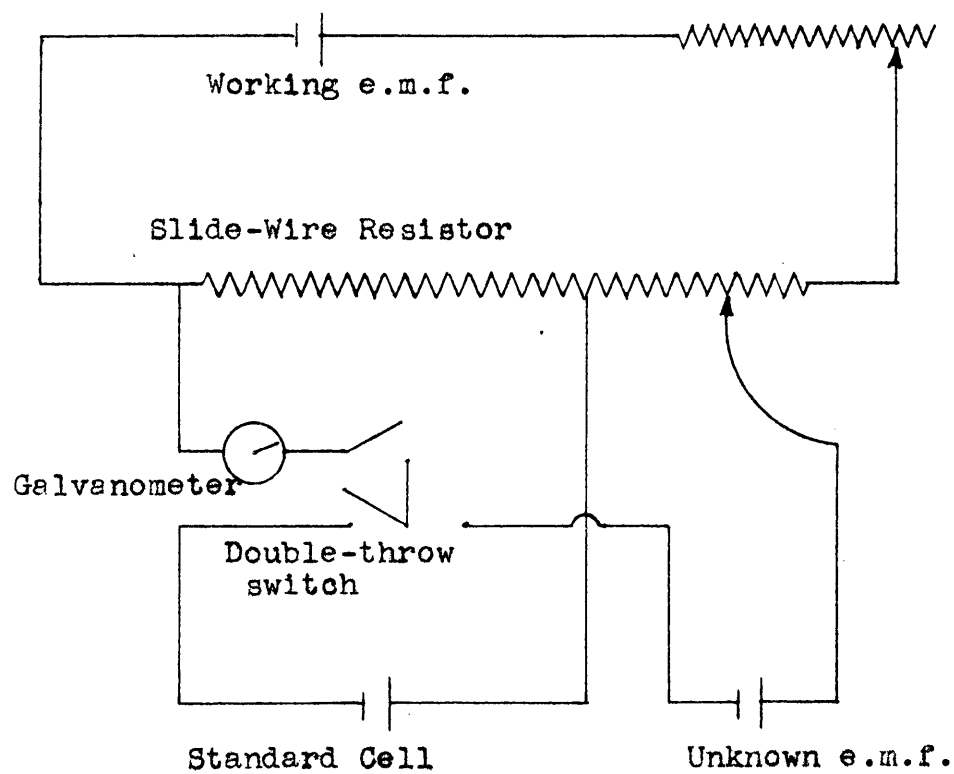
Diagram of Simple Potentiometer Circuit

Fig. 1.

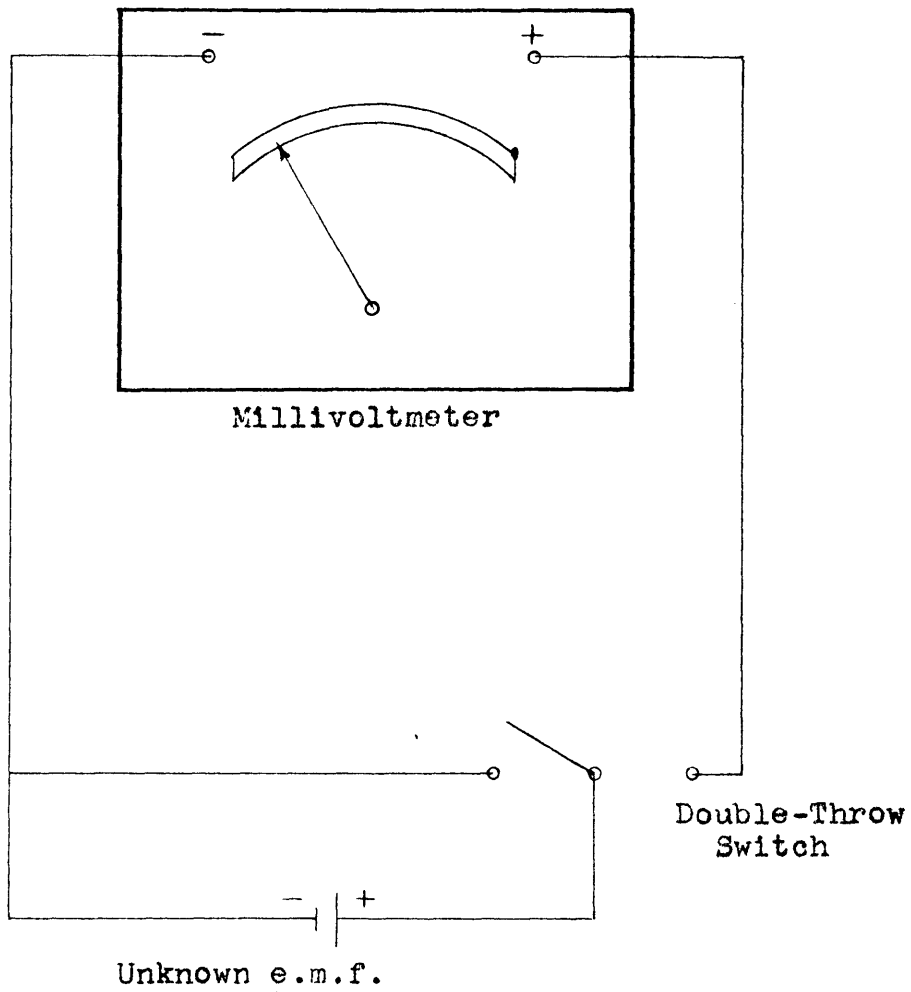
Diagram of Voltmeter Circuit

Fig. 2.

MATERIALSElectrodes

The aluminum-base alloys used were supplied by the Aluminum Company of America. Their designation, nominal analysis, and mechanical condition are given in Table I⁽³⁾.

Table I - Analyses of Aluminum Alloys

Alloy	Nominal Analysis, Percent					Temper
	Al	Cu	Mg	Mn	Other	
2S	99.0					Annealed
3S	98.8			1.2		Annealed
11S	93.5	5.5			Pb 0.5 Bi 0.5	T-3
17S	95.0	4.0	0.5	0.5		T-4
61S	97.9	0.25	1.0		Si 0.6 Cr 0.25	T-6
75S	90.0	1.5	2.5	0.2	Zn 5.5 Cr 0.3	T-7

The copper-base alloys were products of Anaconda Copper Company; and their designation, nominal composition, and degree of mechanical work are given in Table II.

Table II - Analyses of Copper Alloys

Designation	Analysis, Percent		Temper
Bus-bar Copper	Cu	99.9	Annealed
Bus-bar Copper	Cu	99.9	Hard-drawn
Free-Machining Brass	Cu	61.0	Half-hard
	Zn	35.4	
	Pb	3.64	

It must be recognized that only the pure aluminum and pure copper electrodes could present a homogeneous surface, and that in all probability the presence of oxide films would destroy the homogeneity. The alloyed materials would not be homogeneous because of the microconstituents, and the mechanically-worked copper-base materials would probably show varying degrees of cold work in different areas on the specimen.

Electrolytes

Both tap water and distilled water were used as electrolytes. No attempt was made to analyze either one for impurities, and no attempt was made to remove any dissolved gases. Resistivity tests on both tap water and distilled water show the following results:

Tap Water: Approximately 16,000 ohms per
centimeter cube at 18 deg C.

Distilled Water: Approximately 500,000 ohms per
centimeter cube at 18 deg C.

Since the resistivity of any electrolyte is a function of the number and valence but not of the type of ions which it contains, these measurements should be a sufficient basis for reproducing the above electrolytes.

TECHNIQUES

Electrode Preparation

The electrodes were cut to six-inch lengths, and one end was reduced in thickness by filing or grinding until a small spring clip would make good contact with the electrode. The electrodes were marked at a distance of three inches from one end by filing a groove completely around the circumference. One-inch bands of natural-rubber tubing were placed on the upper ends of the electrodes in order to insulate them from the metal clamps which fixed them in position in the electrolyte.

The electrodes were used in three different conditions. These were (1) no preparation, (2) mechanical abrasion with 2/0 emery paper to remove the oxide film, and (3) removal of oxide film in normal sodium hydroxide solution or hydrochloric acid as applicable, followed by a thorough rinse in water.

A comparison of results showed that chemical preparation did not give reproducible values, apparently as a result of non-uniform dissolution of the inhomogeneous materials. A lack of uniformity of readings from unprepared electrodes was probably due to differences in the thickness of the oxide films with differing periods of exposure to air. The mechanical method of preparation was satisfactory, and was subsequently used.

Standardization of Experimental Conditions

By the use of the gauge mark, the electrodes were immersed to a depth of approximately three inches in the electrolyte. A 400 ml. pyrex glass beaker was used to contain the electrolyte, and the electrodes were separated by the maximum possible distance, approximately three centimeters. The following table summarizes the diameters and immersed areas of the electrode materials.

Table III - Electrode Sizes and Areas

Material	Diameter (Inches)	Immersed Area (Square Inches)
2S	0.75	7.50
3S	0.50	4.90
11S	0.75	7.50
17S	0.75	7.50
61S	0.75	7.50
75S	0.75	7.50
Annealed Copper	0.50	4.90
Hard-drawn Copper	0.50	4.90
Brass	0.625	6.18

Temperature conditions were nearly constant within the range 19 deg to 22 deg C. The temperature coefficient of the potentials was neglected by reading only to the nearest millivolt on the potentiometer.

In both the potentiometer and voltmeter circuits the couples were short-circuited to bring them to the polarization potential. The shunt was then removed from the couple, and the first reading was taken. In the potentiometer circuit the couple then remained in open circuit, and readings were made at uniform intervals. In the voltmeter circuit the shunt was restored and was removed only long enough to read

the voltmeter each time.

In a separate experiment the electrodes were immersed but not short-circuited. The disadvantages of this technique will be discussed under the heading "Results."

All experiments were conducted with a quiescent electrolyte. Equipment limitations and reproducibility considerations were responsible for this choice. It may well be that agitation of the electrolyte might affect the results significantly, and future investigators may wish to consider agitation as a variable in their work.

RESULTS

The General Trend

According to McKay and Worthington⁽⁴⁾, the decreasing corrosion rate is characteristic of aluminum and its alloys. This statement was found to be true in the present instance, at least to the extent of varying potentials. In this respect the results agree with those obtained by Kahlenberg and French⁽⁵⁾, whose article, "On the Potential of Aluminum in Aqueous Solutions," emphasizes the fluctuations in the single-electrode potentials of high-purity aluminum.

The usual behavior of the couples, as indicated by potentiometric measurement, was to show an increase in potential to some maximum value after the shunt had been removed. The potential would then reach a comparatively constant value for perhaps fifteen or twenty minutes, then decrease again.

Couples which were not short-circuited had a potential which would start at some maximum value, decrease rapidly at first, then more slowly, and reach a constant value for a short period of time. The potential would then fluctuate again, sometimes increasing and sometimes decreasing with passage of time.

The information obtained from the voltmeter circuit was consistent. The actual voltage reached a peak almost instantaneously, then decreased to a value which changed very slowly with the actual flow of current.

Tabular Summary of Potentials

The following tables summarize the cell potentials between aluminum-base and copper-base electrodes in both tap water and distilled water. Tables IV and V are potentiometer readings, whereas Table VI is composed of voltmeter readings.

Table IV - Open-Circuit Potentials in Tap Water

(Potentiometer Readings)

Aluminum Alloy	Annealed Copper (Volts)	Hard-drawn Copper (Volts)	Half-hard Brass (Volts)
2S	.440	.420	.425
3S	.380	.415	.350
11S	.290*	.325	.260
17S	.340	.325	.310
61S	.455	.440	.410
75S	.430	.400	.390

*Average of scattered values

Table V - Open-Circuit Potentials in Distilled Water

(Potentiometer Readings)

Aluminum Alloy	Annealed Copper (Volts)	Hard-drawn Copper (Volts)	Half-hard Brass (Volts)
2S	.440	.425	.427
3S	.420	.420	.330
11S	.285*	.355	.264
17S	.305	.350	.250
61S	.441	.375	.358
75S	.430	.405	.380

*Average of scattered values

Table VI - Polarized Potentials in Tap Water

Aluminum Alloy	(Voltmeter Readings)		
	Annealed Copper (Millivolts)	Hard-drawn Copper (Millivolts)	Half-hard Brass (Millivolts)
2S	0.6	0.4	1.0
3S	0.5	0.3	1.2
11S	0.4	0.7	0.3
17S	0.3	0.7	0.4
61S	0.5	0.7	0.9
75S	0.6	1.0	0.5

Discussion

Open-Circuit Potentials: The effect of surface preparation on the behavior of the potentials is more noticeable when a graph of potential versus time is made. When the electrodes were not prepared, a steadily decreasing potential was noted in each case, and occasionally no steady value would be noticed. For both mechanical and chemical surface preparation, if the couple were not short-circuited, some maximum value of potential would be attained almost instantaneously, followed by a decrease in potential at a decreasing rate. A relatively constant potential value would finally be reached.

When the couples were short-circuited before any readings were taken, the values obtained were usually low at the start, but rose to some maximum, then decreased again to some equilibrium value. This behavior was true for both chemical and mechanical preparation of the electrodes.

A phenomenon which occurred several times with alloy 75S involved a steadily increasing potential which could not be reduced to the normal range of values by short-circuiting the cell. Values of over 0.9 volt were maintained for more than

ten minutes at a time. This behavior might be attributed to the exposure of active constituents at the surface of such a complex alloy.

When the electrolyte was stirred in the immediate vicinity of the electrodes, the potential was immediately disturbed. When the solution again became quiet, the potential would approach its former value. The reason is probably that agitation affects the net rate of diffusion of the metal ions from the metal into the solution.

Polarized Potentials: The voltmeter circuit gave results which, it is believed, were indicative of actual corrosion rates. The values which were obtained checked within the limits of accuracy of the instrument used, and little difference was seen in the results whether the electrodes were prepared mechanically or chemically.

The cell voltages were much lower when distilled water was used as the electrolyte than when tap water was used. No polarized potentials are recorded for a distilled-water electrolyte because the indicated readings on the voltmeter were much smaller than the possible error.

General Summary

The tabular summary of potentials reveals the behavior of three different types of galvanic couples. The values obtained using annealed copper and hard-drawn copper show small variations for the same aluminum alloy. These variations are not conclusive evidence that a difference in single-electrode potential exists between annealed and hard-drawn copper. Such a difference may have been minimized by the mechanical work

done in cleaning the surface of the annealed copper electrode.

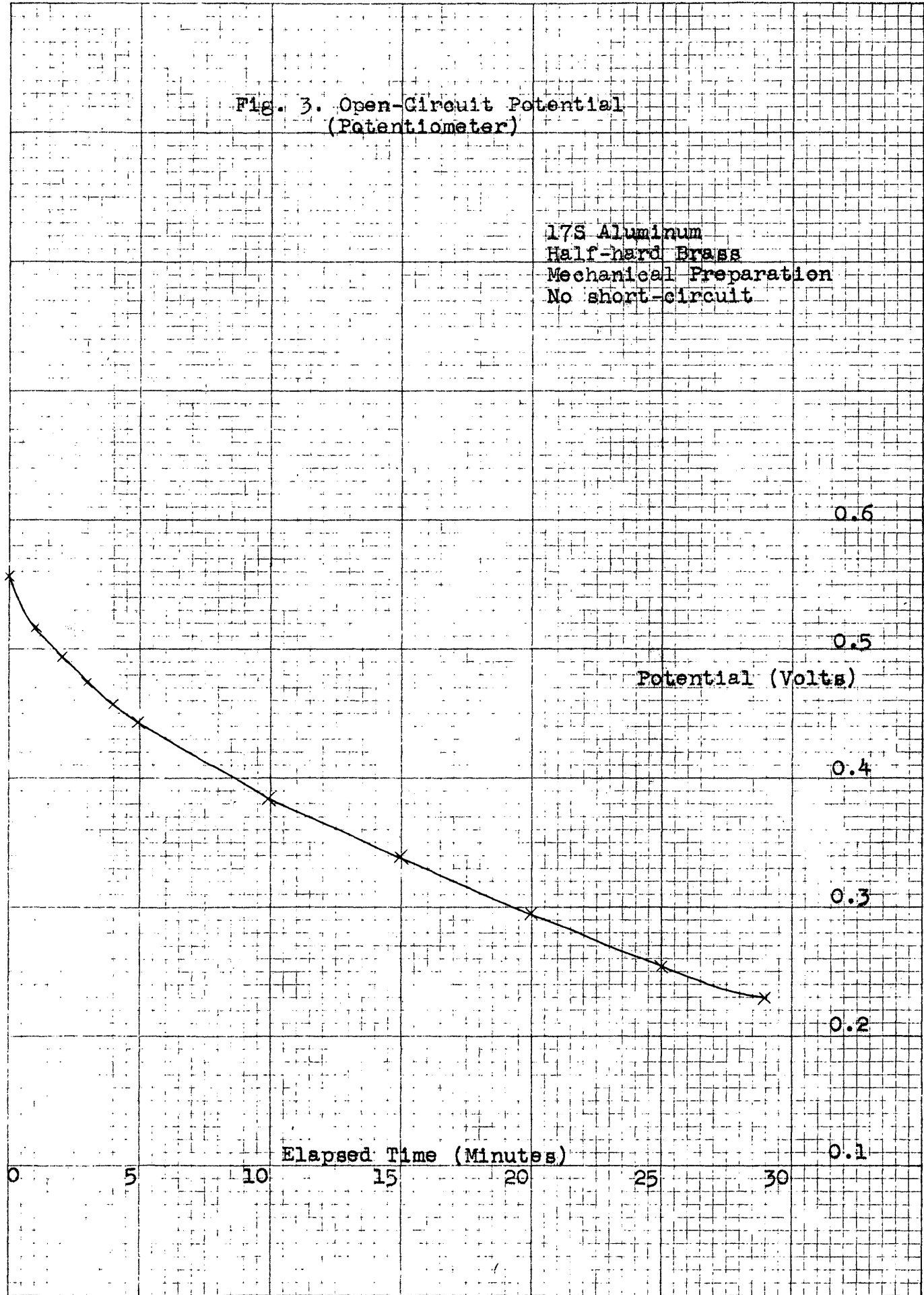
The potentials obtained by the use of a brass electrode are somewhat lower than those shown with copper electrodes. The presence of a large percentage of zinc in the material tends to reduce the hydrogen overvoltage of the electrode.

A comparison of the different values of polarized potentials has little meaning because of the order of magnitude of the possible error.

The following graphs of potential versus time will show how the method of preparation affects the rate and manner of attaining a steady state.

Fig. 3. Open-Circuit Potential
(Potentiometer)

17S Aluminum
Half-hard Brass
Mechanical Preparation
No short-circuit



Elapsed Time (Minutes)

Potential (Volts)

0

5

10

15

20

25

30

0.1

0.2

0.3

0.4

0.5

0.6

Fig. 4. Open-Circuit Potential
(Potentiometer)

75S Aluminum
Annealed Copper
Mechanical Preparation
Cell short-circuited

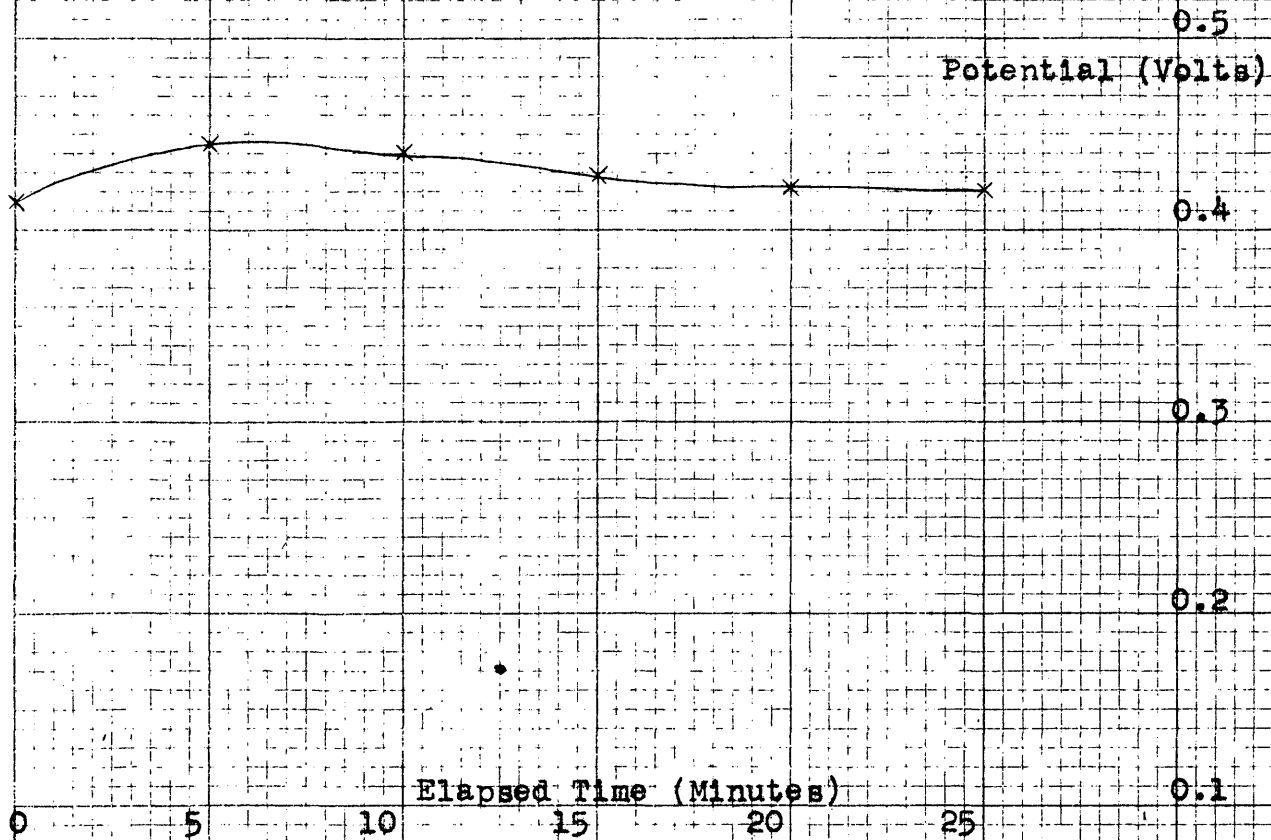


Fig. 5. Open-Circuit Potential
(Potentiometer)

3S Aluminum
Annealed Copper
Chemical Preparation
No short-circuit

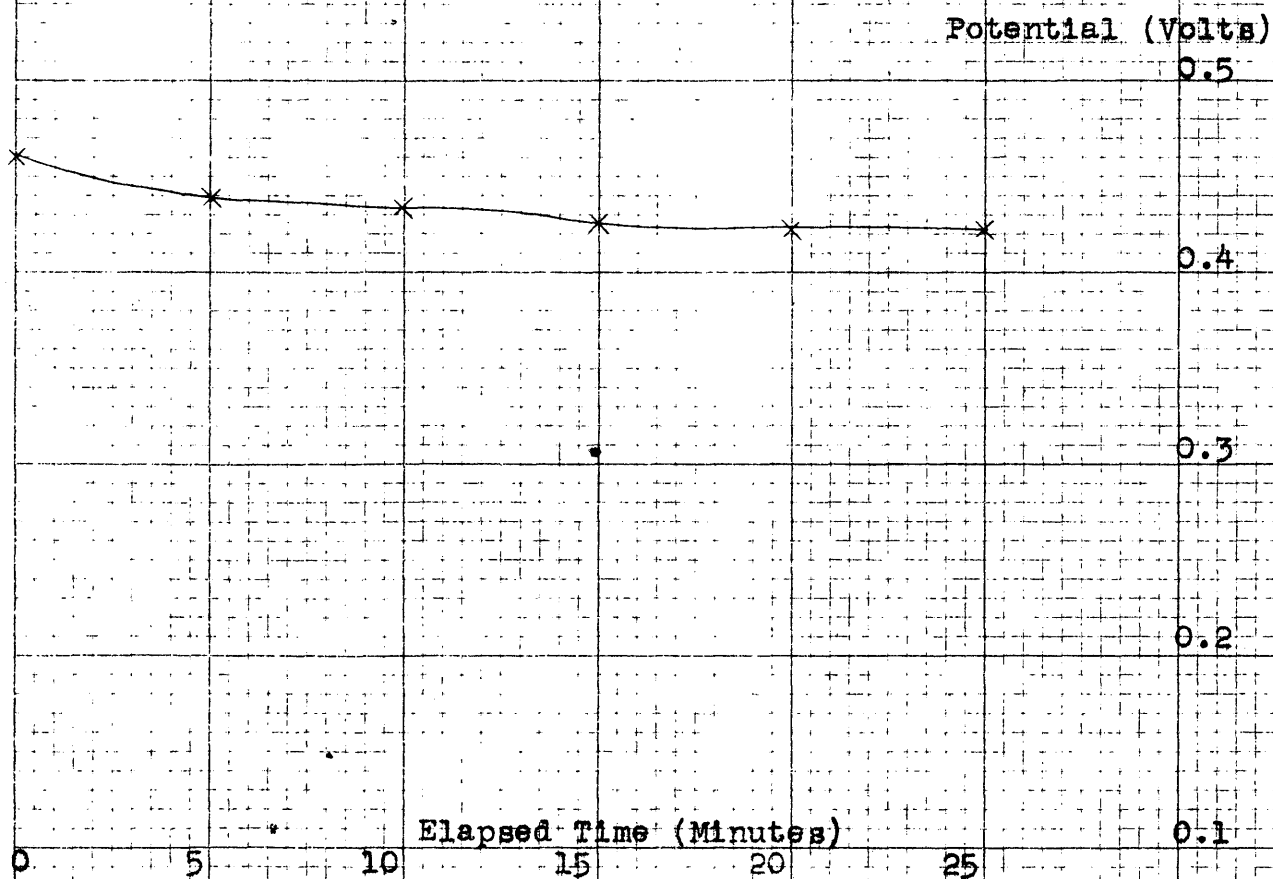


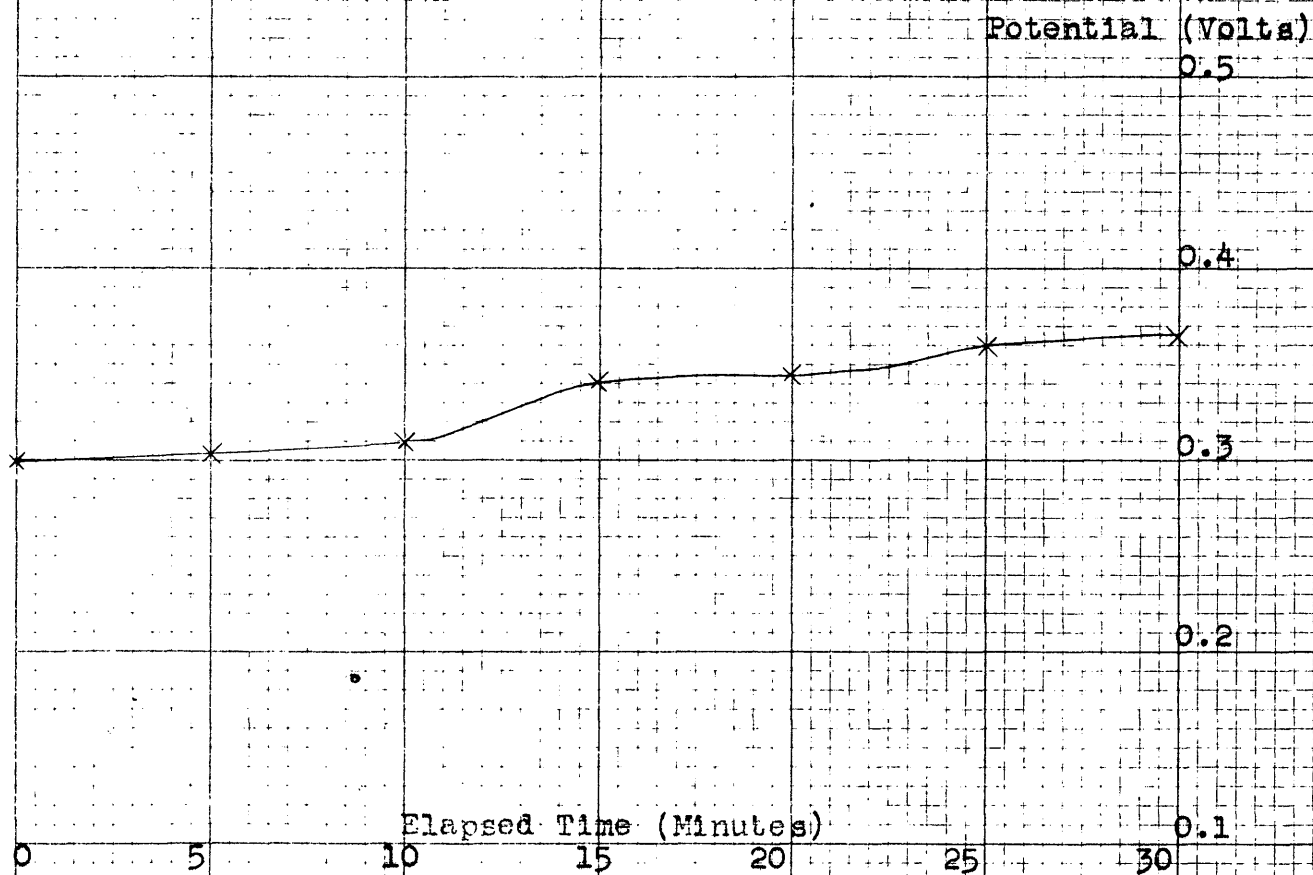
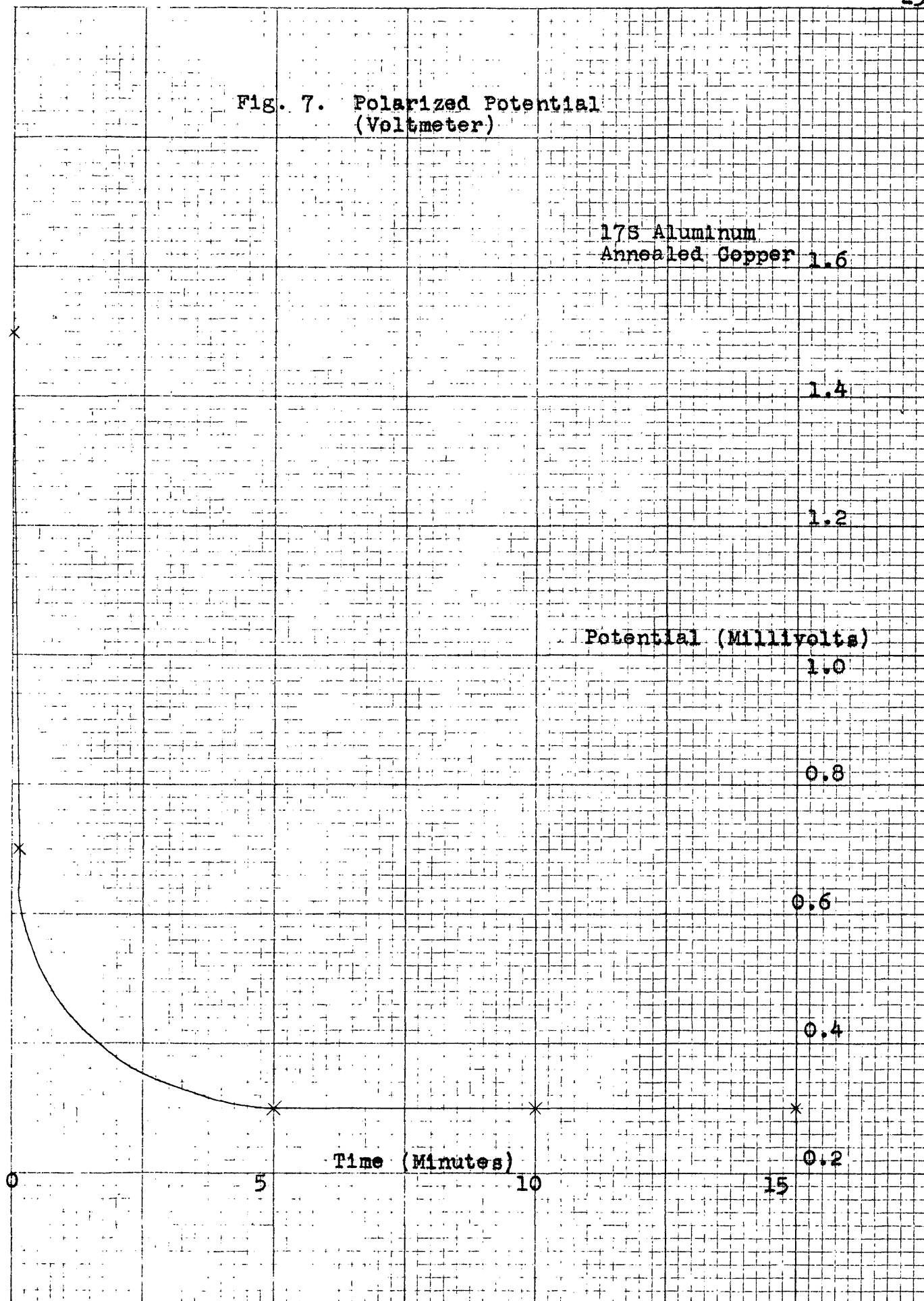
Fig. 6. Open-Circuit Potential
(Potentiometer)3S Aluminum
Annealed Copper
Chemical Preparation
Cell short-circuited

Fig. 7. Polarized Potential
(Voltmeter)

CONCLUSION

Analysis of Experimental Work

A study of the data obtained in this work indicates several significant facts. More data were obtained on open-circuit potentials than on polarized potentials. It is entirely probable that the information on open-circuit potentials is also more accurate than the values obtained for polarized potentials. The physical significance of the open-circuit potential as applied to actual corrosion rates is rather uncertain, however.

Polarized potentials of galvanic cells using tap water as an electrolyte have been shown to have a measurable and relatively constant value over at least a short period of time. The equipment needed to measure these potentials is easily obtained and simple to use.

The most serious deficiency in this work, perhaps, is the lack of correlation between laboratory results and corrosion rates as determined in actual use. If such correlation were to be made, it would be necessary to consider also the effects of agitation, inhibitive films, and films which tend to promote corrosion. The effect of dissolved impurities would ordinarily be shown as an increase in the value of the polarized potential. It must be emphasized, however, that this method is not applicable to measuring rates of corrosion by local galvanic action.

Modifications of Equipment

In order to facilitate the study of this problem in the laboratory, a recording-type voltmeter would be useful. The curve which such an instrument gives would lend itself to rapid interpretation of results, and extended studies of polarized potentials versus time could be made readily.

For measurements of potentials in the field, a portable voltmeter of the type employed in this work would probably be satisfactory, and would give results which could be compared with those obtained in the laboratory. At the same time, actual known corrosion rates could be correlated with these polarized potentials.

Further Investigations

The applicability of this technique to industrial problems can be determined only by further work. Such a project would consist of two different lines of investigation.

The laboratory work should entail a study of the galvanic couples which are commonly found in industry and an investigation of the electrolytes which are actually encountered. Extended time-potential studies would allow the evaluation of corrosion rates in terms of the recorded polarized potentials.

The second part of the work would, of necessity, be done in the field. This work would involve searching for suspected galvanic couples by means of the portable voltmeter circuit previously described. Measurements of polarized potentials of known couples could also be taken, as additional aid in evaluating the laboratory work.

In theory, the technique looks promising. Its success or failure in practice can be determined only by thoroughly investigating its possibilities.

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