# THE EFFECT OF MAGNESIUM IONS ON THE CURRENT EFFICIENCY OF MAGNESIUM ANODES USED AS CATHODIC PROTECTORS

By

Daniel Smith Hawxhurst

A Thesis Submitted to the Graduate Committee
In Partial Fullfillment of the Requirements For the Degree of

MASTER OF SCIENCE

in

CHEMISTRY

Approved:

Thesis Advisor

Head, Department of Chemistry

Dean of the College

Chairman, Graduate Committee

Virginia Polytechnic Institute

1947

## ACKNOWLEDGEMENTS

The author wishes to express his gratitude for the helpful suggestions and criticisms given him by Dr. E. F. Furtsch and Dr. J. A. Addlestone during this investigation. He also wishes to thank Dr. J. W. Murray for his assistance in the construction of part of the equipment used.

Daniel S. Hawxhurst

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# INTRODUCTION

It has long been known that, when two dissimilar metals are in electrical contact with each other in an electrolytic environment, the metal with the lower solution potential will be spared from corrosion at the expense of the other. Zinc has been used for perhaps 50 or 75 years for protection of marine installations. Recently, however, the trend has been toward the use of magnesium anodes. This has been due to the fact that magnesium has both a higher electrochemical equivalent and a higher solution potential than zinc, and to the fact that the price of magnesium has decreased to the point where economics permits its use.

A great deal of research has already been done in developing the use of magnesium for cathodic protection, and it is the purpose of this paper to add certain facts to that store of knowledge already gained.

## THEORY

There is a certain inherent tendency among all metals, when exposed to the elements, to revert to one or another of the forms in which they were originally found in the earth. This is due to the general tendency for any substance to change from a given state to another state having greater stability.

Speller[1] defines corrosion as "the chemical action of environment resulting in deterioration and destruction". This action is usually superficial, but it is often more pronounced along grain boundaries or other lines of weakness.

According to Burns[2], corrosion in the presence of moisture is an electrolytic process in which the metal dissolves at certain areas or points. These areas or points are the anodes of small corrosion cells; the cathodes are adjacent areas on the metal surface at which hydrogen is deposited. The driving force or potential difference of these cells arises either from some physical or chemical inhomogeneity of the metal or from some inhomogeneity of the environment. This electrolytic operation is influenced by such factors as composition, size, and distribution of the anodic and cathodic areas, the character of the products of corrosion and the chemical nature and conductance of the surrounding environment.

Any metal above hydrogen in the electromotive series will replace hydrogen ions in an electrolytic environment. This hydrogen forms a protective film over the metal and thus slows the rate of corrosion. Hence, in ordinary corrosion processes, the rate at which the film of hydrogen is removed will, to a large extent, determine the rate of corrosion. The hydrogen may be removed either by evolution in the gaseous form, by cathodes operating at low overvoltage, or by combination with oxygen or other oxidizing materials[2].

If two different metals are in electrical contact with each other in an electrolytic environment, the one which is the more anodic will have a tendency to corrode faster than it normally would, while the metal which is the more cathodic will not corrode as fast. This is due[1] to the fact that any metal which is above hydrogen in the electromotive series and which does not quickly form an impermeable protective coating when placed in solution, will tend to plate out a film of hydrogen on any other more cathodic material which is in electrical contact in solution.

The electromotive series, however, is not always dependable as a basis for predicting which metal of any couple will suffer galvanic attack when exposed to any solution. The reason for this, according to Mears and Brown[3], is that the solution potential of the different metals will alter as the solution in which they are exposed is changed. Thus it is necessary to measure the potential of the metals in the particular solution under consideration.

The potential difference between the two metals is a measure of the driving force tending to cause corrosion currents and will indicate which of the two metals will be anodic[4], but the magnitude of these currents is the only true measure of the velocity of attack. Large currents are not necessarily associated with large potential differences, since the film formation or polarization controls this to a large degree.

The relative areas of the two metals, of which the couple is composed, is an important factor, since a large ratio of cathode area to anode area, will result in high current density on the anode, and a consequent high rate of corrosion.

From the above considerations, it can be seen that one method of protecting subsurface structures would be by a method which has become known as "Cathodic Protection". In this method, a direct current of electricity is passed from the cathode, or structure to be protected, to some expendable anode buried in the vicinity of the cathode. The cathode will then be protected at the expense of the anode. This current may either be obtained from an outside source such as a battery or a rectifier, or it may be produced by the potential difference between the anode and cathode itself. If the source is external, the anode may consist of any kind of scrap metal, but if the source is internal, the anode must be made of a metal which is relatively high in the electromotive series.

Probably one of the best examples of cathodic protection, is the use of zinc strips to prevent the corrosion of the propellors and rudders of ships. Here large strips of zinc are bolted directly to the parts to be protected, and may be replaced periodically or whenever they are worn out. This is a very necessary part of the construction since not only is sea-water highly corrosive, but the use of bronze bearings in the moving parts causes about a forty percent increase in the normal corrosion rate.

According to Mears and Brown[5] there are certain facts which must be considered in the use of cathodic protection. In the first place, if the protection is to be complete, the cathode must be polarized to a potential which is at least as great as the open circuit potential of the anodes. Also, the current required for complete protection will depend upon the current required to polarize the cathode to a potential equal to or more anodic than the open circuit potential of the anodes.

Corrosion may in some cases be increased by products of electrolysis. For instance[6], stainless steel is not attacked appreciably by a 0.5% solution of sulfuric acid. However, when aluminum is coupled with stainless steel, the steel becomes badly corroded. This is due to the fact that the hydrogen which is deposited on the cathode reduces the protective oxide film coating on the stainless steel and allows corrosion to proceed.

F. M. Ruffing [7] states that in order to have effective cathodic protection by use of a galvanic anode, the latter must have a potential and a current capacity high enough to neutralize the anodic areas on the metal to be protected.

Magnesium has the relatively high theoretical electrochemical equivalent of about a thousand ampere hours per pound and a solution potential against a copper sulfate half cell of 1.6 to 1.7 volts, depending on whether pure magnesium or an alloyed material is used. In comparison, zinc has an electrochemical equivalent of 372 ampere-hours per pound and a solution potential of approximately 1.1 volt.

Laboratory and field experiments have shown that the efficiency and life of a magnesium anode is largely dependent upon three factors: (1) the composition of the metal used, (2) the backfill or electrolyte used around the anode, and (3) the current density at which the anode operates. It has been found that the current density giving the best efficiency and results is about 0.5 milliampere per square inch[7,8].

The term "current efficiency" as used is the ratio of the theoretical quantity of electricity which could be produced to that actually produced by the corrosion cell[9]. It is expressed in terms of percent efficiency.

H. A. Robinson[10] concludes that both the current efficiency of the anode and the uniformity of the anode consumption will generally improve with increase in the current density. He obtained efficiencies of 50 to 60 per cent with magnesium alloy anodes operating at current densities of 3.5 to 7.0 milliamperes per square inch, but found that local corrosion increased with increased current density so that the current efficiency is limited to 65 to 70 per cent. He also found that in general, changes in magnesium ion concentration in the electrolyte have no signifigant effect upon the efficiency of the anode except in cases where the magnesium ion concentration is very high. He states that a high concentration of magnesium ion will reduce the efficiency of the anode by buffering the electrolyte and that this effect is greatest when pure magnesium anodes are used.

## THE INVESTIGATION

Object. The object of this investigation was to determine, if possible, whether or not the magnesium ion concentration in the backfill has a signifigant effect upon the current efficiency of a pure magnesium anode when used to protect a steel cathode. According to H. A. Robinson[10], there should normally be no effect, but he indicated that there is room for doubt in some cases.

Apparatus and Material. The apparatus consisted of a corrosion or galvanic cell using pure bar magnesium for the anode and hot-rolled bar steel for the cathode. This was connected in series with two decade resistance boxes, a milliammeter, a copper coulometer and a single-pole-single-throw switch. A double-pole-double-throw switch was used, as shown in Fig. 1, so that the potential difference of the corrosion cell and the potential versus a copper half-cell could be measured at the end of each run.

The electrodes were placed in an artificial backfill composed of Pennsylvania flint ground to 200 mesh. A small amount of sodium sulfate was added to this to increase the conductance. The entire cell was kept saturated with water.

The cathode used was a bar of hot-rolled steel, six inches long and one inch in diameter. The lead was soldered to this, and the junction covered with a coating of paraffin to prevent local corrosion.

The anodes were pure magnesium bars about a half inch in diameter and four inches long.

The copper sulfate half cell was constructed, as shown in Fig. 2, using a large test tube containing a saturated solution of copper sulfate in which was suspended a copper electrode. The salt bridge consisted of a one per cent solution of ammonium nitrate. Agar-agar containing a small amount of ammonium nitrate solution was used at the junction between the copper sulfate and ammonium nitrate solution. A separatory funnel was used to hold the supply of $NH_4NO_3$ solution to be used and the rubber tube was used so that the tip of the bridge could be placed in any position without moving the rest of the equipment. Ammonium nitrate, rather than potassium chloride, was chosen as the electrolyte because of the highly corrosive nature of the chloride ion.

The potentiometer used was a Type K-2, number 7552, made by Leeds and Northrup Co. Used with the potentiometer was a D'Arsonval galvanometer, number 2500, and a lamp and scale, number 2100, also made by Leeds and Northrup Co.*

Method of Procedure. The magnesium anode was machined down to a smooth surface, thus removing all pits and other irregularities on the surface of the metal and giving a constant diameter. The diameter was then measured by means of calipers and the average

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*A complete description of this apparatus may be found in "Potentiometric Measurements of Corrosion", a B. S. thesis by Donald Mohler. (March 1943) diameter recorded. It was then weighed and the weight recorded. The ends of the anode were then coated with lacquer number G-1114A, manufactured by the Gordon-Lacey Chemical Products Company. This was done to prevent excess local corrosion at the sharp edges. The lead was attached immediately by means of a universal spring clip, making sure of good electrical contact. It was then hung up to dry, After drying, the length of the uncoated portion was measured and recorded. From the length and diameter, the area of the bare anode was calculated.

The copper cathode of the coulometer was cleaned with fine emery paper and then with 1:1 nitric acid and washed with distilled water. It was then dried with acetone and placed in a desiccator for at least one hour, after which it was weighed and the weight recorded. The cathode was then placed in the coulometer and the proper connections made.

The anode was placed in the corrosion cell as shown in Fig. 1. In placing the anode in the cell, care was taken to see that the artificial soil was packed firmly around the anode and that all of the uncoated portion was covered. All of the electrical connections were then checked, the switch (S) was closed and the time recorded.

Throughout the run, the current was held at a constant value approximately equal to one half of the numerical value of the area in square inches, by means of the variable resistance ($R_2$). This required constant attention during the first five or six hours because the current tends to decrease until the cathode becomes polarized. After this time, however, it is only necessary to check and adjust the current every hour or two during the remainder of the 24-hour run.

At the end of 24 hours, the circuit was broken by opening switch S and the cathode allowed to depolarize. Then the double-pole-double-throw switch (D) was placed in the "down" position, thus placing the potentiometer in the circuit with the cathode and the copper sulfate half cell. The glass tip of the half cell was then placed against the steel cathode and the potential measured on the potentiometer and recorded. Switch "D" was then placed in the "up" position and the difference in potential between the anode and cathode was measured and recorded. Since with a Type K-2 Potentiometer, open circuit potential differences of greater than 1.6 volts cannot be measured, the half-cell potential difference between the magnesium anode and the copper sulfate half-cell were determined by adding together the potential differences Mg versus Fe and Fe versus Cu.

After removing the anodes from the cell, the loose corrosion product was brushed off in a stream of running water. This was followed by immersion in agitated 20 per cent chromic acid solution containing one per cent silver nitrate, to remove the residual corrosion products. The anode was then rinsed and the lacquer removed with acetone, after which it was dried and reweighed.

The copper cathode was removed from the coulometer, washed with distilled water, dried and weighed. From the gain in weight,

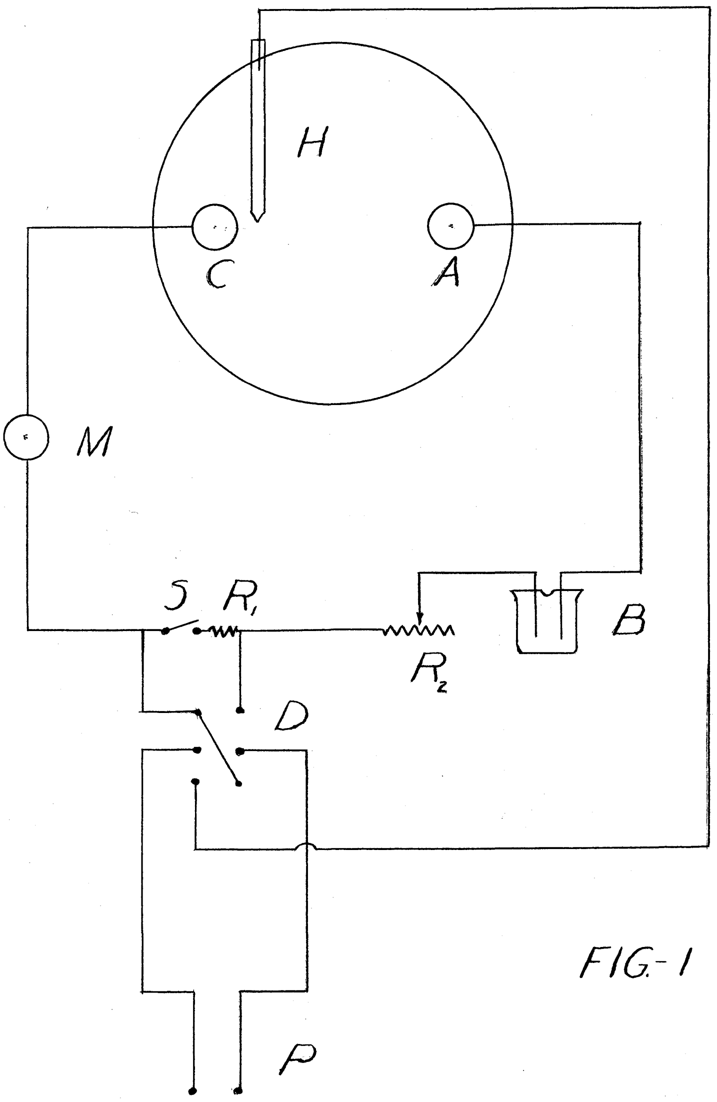

FIG.-1

P-Potentiometer
B-Coulommeter
$R_1$-Standard Resistance
$R_2$-Variable Resistance
H-Copper Sulfate Half Cell
C-Cathode
A-Anode
S-Switch
D-Double-pole-Double-throw Switch
M-Milliammeter

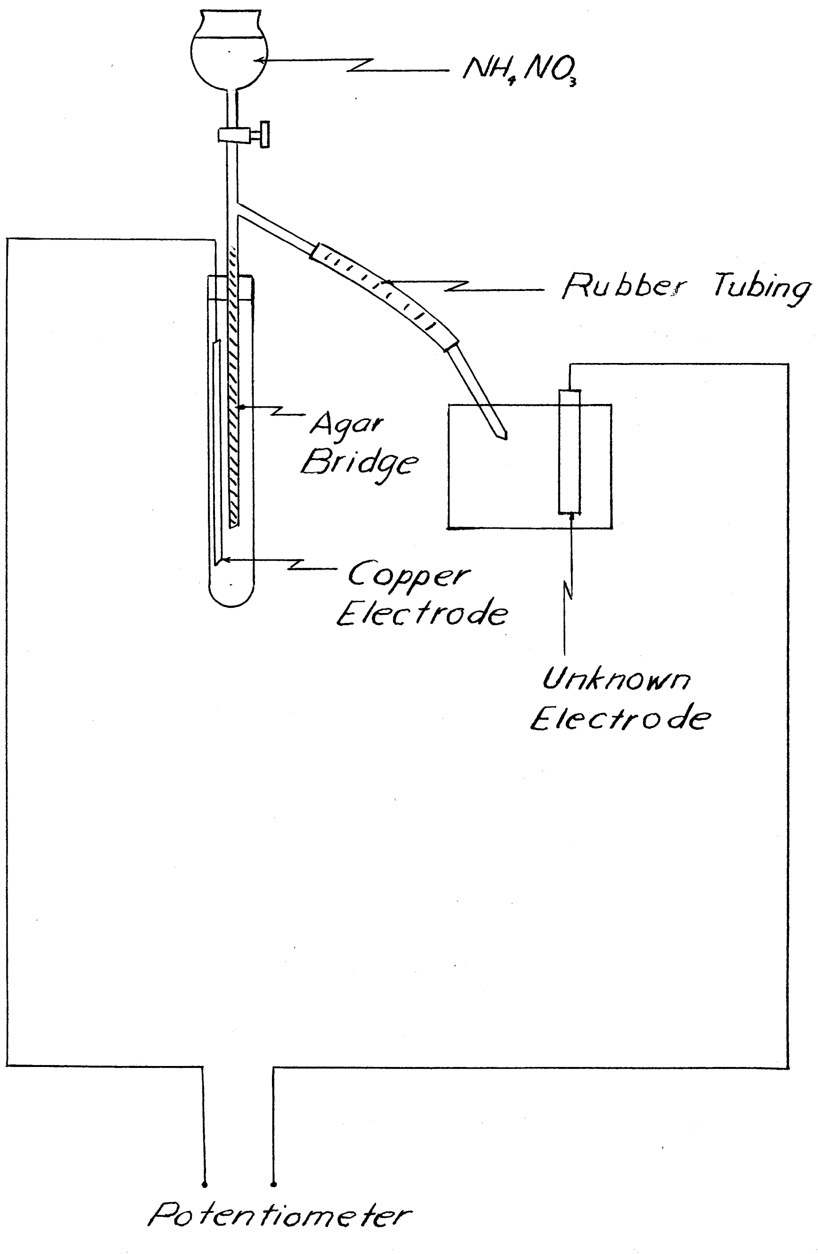
$NH_4NO_3$
Rubber Tubing
Agar Bridge
Copper Electrode
Unknown Electrode
Potentiometer

FIG-2

the amount of current passed and the average current were determined.

The current efficiency of the magnesium anode was then calculated from the equation

$$\frac{\text{atomic wt. of Mg X Cu gain}}{\text{atomic wt. of Cu X Mg loss}} \times 100 \; - \; \text{current efficiency}$$

Two sets of runs were made in the course of the experimental work. The first set, due to an error, was done with the cell containing approximately fifty grams of manganese sulfate. This error was discovered soon after it was made, but it was decided that this would not affect the final analysis of the results, since the object of the experiment was to obtain relative values of current efficiency for various concentrations of magnesium ion in the cell. This contention was verified by making an entirely new set of runs after complete removal of the manganese sulfate. There was no signifigant difference in the data of the two sets of runs. In each set, the magnesium ion concentration was increased after every other run by adding to the cell a concentrated solution of 25 grams of magnesium sulfate in distilled water.

Results. The data obtained from the experimental work are shown in Tables 1 and 2. Table 1 contains the data obtained from the first set of runs in which the manganese sulfate was added by mistake. Table 2 contains the data obtained from the second set of runs. In the lower part of each table are data from runs in which the current density was relatively high.

On Chart 1, the current efficiency of the anode was plotted

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against the concentration of magnesium sulfate in the cell. The addition of ten grams of magnesium sulfate to the cell represents an increase in the magnesium ion concentration of approximately one per cent.

Charts 2 and 3 were obtained by plotting current against time with the total resistances held at constant values of 100 ohms and 1 ohm, respectively.

# TABLE 1

## DATA FOR FIRST SET OF RUNS

| Area of Anode | Magnesium Loss | Copper Gain | Average Current | Current Density | Current Efficiency | Potential Cu vs Mg | Total $MgSO_4$ Added |
|---|---|---|---|---|---|---|---|
| sq. in. | gms. | gms. | MA. | $MA/in^2$ | percent | volt | gms. |
| 6.10 | 0.1531 |  | 2.98 | 0.48 | 43 | 1.745 |  |
| 5.58 | 0.0658 | 0.0703 | 2.47 | 0.444 | 41 | 1.653 |  |
| 5.23 | 0.0620 | 0.0781 | 2.71 | 0.519 | 48 |  |  |
| 5.71 | 0.1135 | 0.0795 | 2.8 | 0.491 | 27 | 1.64 |  |
| 4.82 | 0.1007 | 0.0823 | 2.9 | 0.601 | 31 | 1.64 |  |
| 5.36 | 0.1151 | 0.0772 | 2.72 | 0.508 | 26 | 1.647 | 25 |
| 5.25 | 0.0834 | 0.0674 | 2.37 | 0.452 | 31 | 1.678 | 25 |
| 6.17 | 0.1115 | 0.758 | 2.66 | 0.432 | 26 | 1.669 | 50 |
| 5.17 | 0.0789 | 0.0684 | 2.40 | 0.465 | 33 | 1.633 | 50 |
| 6.00 | 0.1149 | 0.0830 | 2.91 | 0.486 | 29 | 1.664 | 75 |
| 5.90 | 0.0909 | 0.0788 | 2.76 | 0.468 | 33 | 1.675 | 75 |
| 5.55 | 0.1026 | 0.0719 | 2.49 | 0.449 | 27 | 1.643 | 100 |
| 5.74 | 0.1099 | 0.0698 | 2.47 | 0.431 | 24 | 1.647 | 100 |
| 5.64 | 0.1265 | 0.0728 | 2.56 | 0.454 | 22 | 1.655 | 125 |
| 5.76 | 0.0989 | 0.0807 | 2.84 | 0.494 | 31 | 1.659 | 125 |
| 4.80 | 0.1285 | 0.1718 | 6.03 | 1.257 | 51 |  |  |
| 5.32 | 0.2136 | 0.4111 | 14.44 | 2.72 | 74 |  |  |
| 5.26 | 0.1482 | 0.1694 | 5.96 | 1.142 | 44 |  |  |

## TABLE 2

## DATA FOR SECOND SET OF RUNS

| Area of Anode | Magnesium Loss | Copper Gain | Average Current | Current Density | Current Efficiency | Potential Cu vs Mg | Total $MgSO_4$ Added |
|---|---|---|---|---|---|---|---|
| sq. in. | gms. | gms. | MA. | $MA/in^2$ | percent | volt | gms. |
| 5.10 | 0.1387 | 0.0997 | 3.51 | 0.688 | 27 | 1.620 | |
| 4.59 | 0.0536 | 0.0602 | 2.12 | 0.463 | 43 | 1.628 | |
| 4.92 | 0.0827 | 0.0719 | 2.75 | 0.560 | 36 | 1.619 | 25 |
| 5.86 | 0.0917 | 0.0759 | 2.67 | 0.458 | 32 | 1.621 | 25 |
| 5.27 | 0.1131 | 0.0706 | 2.48 | 0.472 | 24 | 1.630 | 50 |
| 5.60 | 0.1388 | 0.0740 | 2.60 | 0.465 | 20 | 1.627 | 50 |
| 5.10 | 0.0902 | 0.0714 | 2.51 | 0.493 | 30 | 1.625 | 75 |
| 5.23 | 0.0911 | 0.0781 | 2.75 | 0.526 | 33 | 1.625 | 75 |
| 4.84 | 0.1102 | 0.0755 | 2.65 | 0.549 | 26 | 1.624 | 100 |
| 5.10 | 0.1076 | 0.0753 | 2.65 | 0.520 | 27 | 1.626 | 100 |
| 4.15 | 0.2199 | 0.2340 | 8.24 | 1.984 | 41 | 1.623 | |
| 4.09 | 0.1799 | 0.2474 | 8.71 | 2.130 | 53 | 1.617 | |

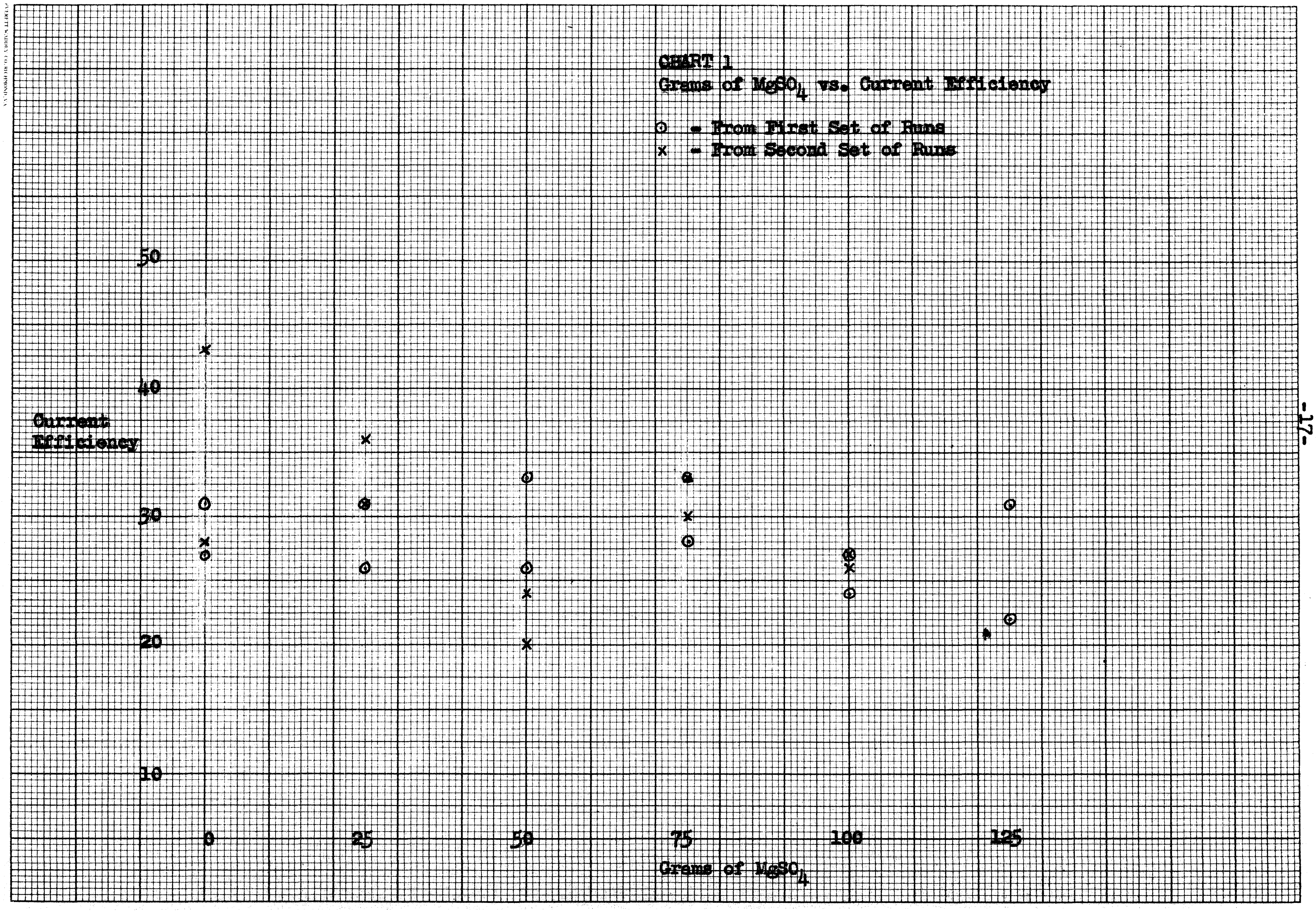

CHART 1
Grams of $MgSO_4$ vs. Current Efficiency

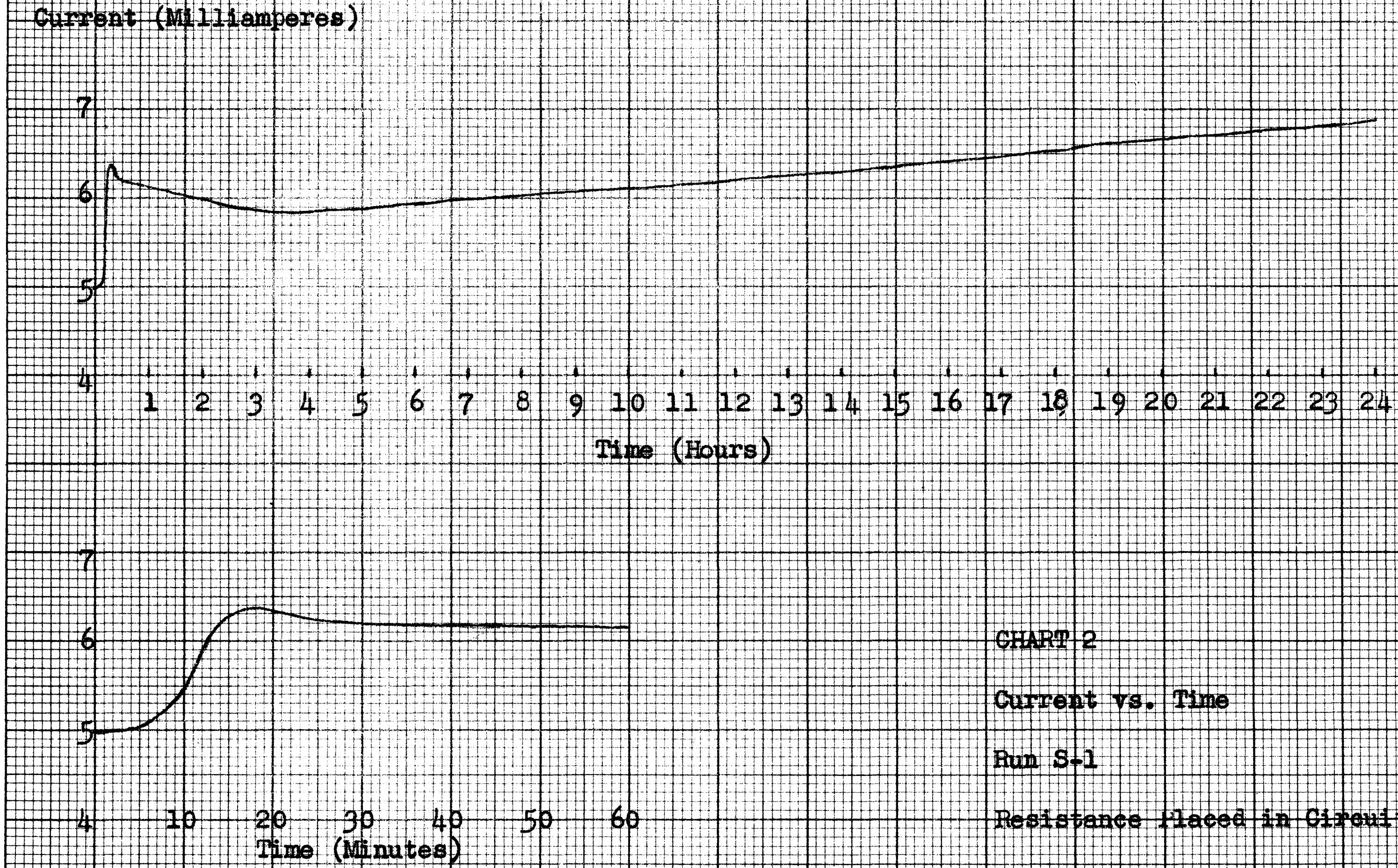

CHART 2

Current vs. Time

Run S-1

Resistance Placed in Circuit - 100 ohms

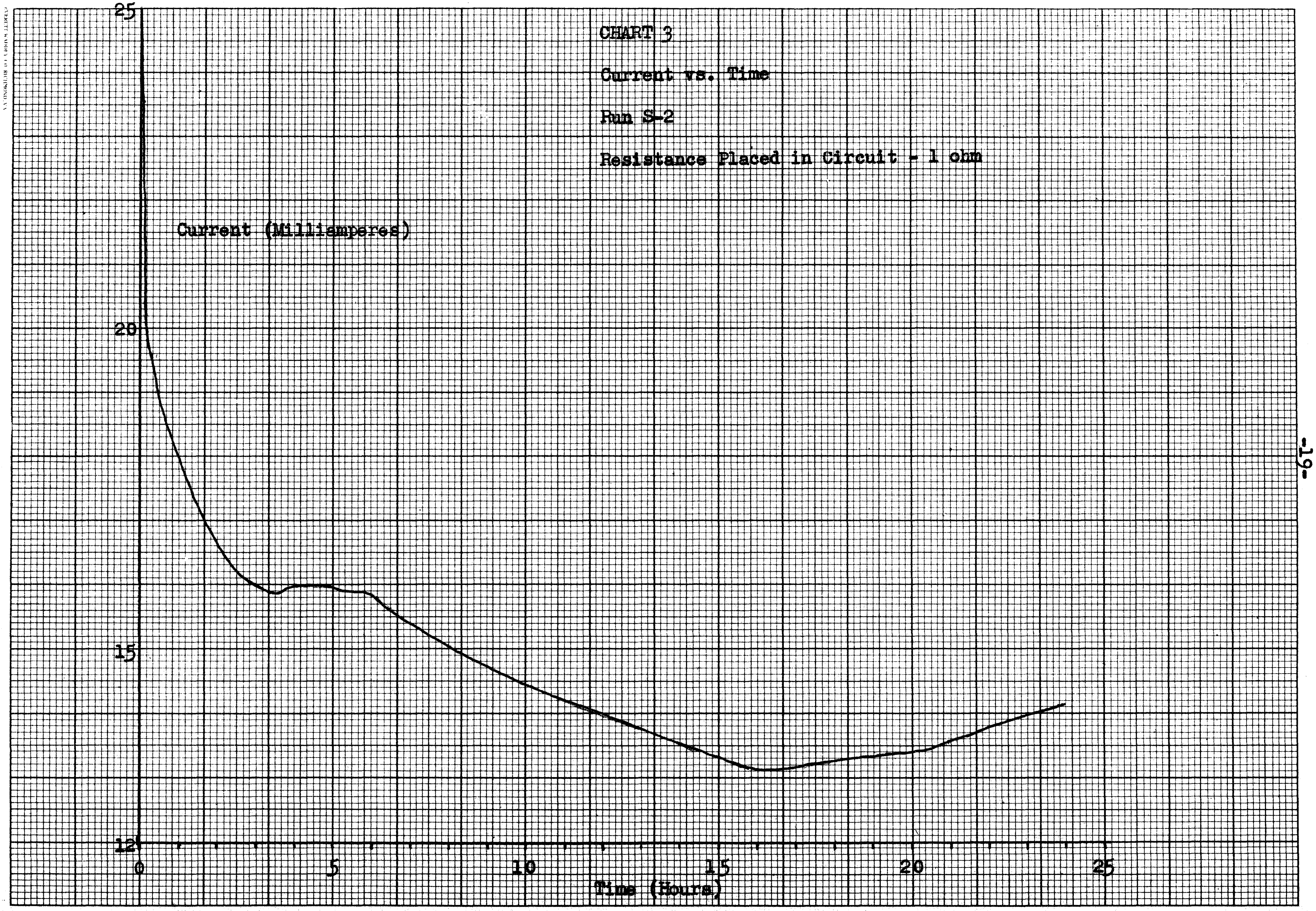

CHART 3

Current vs. Time

Run S-2

Resistance Placed in Circuit - 1 ohm

# DISCUSSION OF RESULTS

A statistical analysis of the results obtained from the two sets of runs, shows that the presence of the manganese sulfate had no signifigant effect upon the current efficiency of the magnesium anode. This was determined by making use of "Student's _t_ test".[11] Therefore it was possible to combine the data obtained from the two sets of runs. Furthermore, it was evident from examination, that the current efficiency obtained in the third run of the second set, was of no value in the consideration of the results. It was, however, not disregarded in the statistical analysis.

Examination of Tables 1 and 2 and Chart 1 shows that, under the conditions of this experimental work, the increase in the concentration of magnesium ion had no appreciable effect on the current efficiency of the magnesium anode. This conclusion is verified by a complete statistical analysis of the results shown in the two tables. There was a great deal of variation, however, in the results obtained. The average variation was 3.99 per cent.

The data shown in the lower part of each of the Tables indicate that there was a relation between current efficiency and the current density at which the anode operated. In both sets of runs, the current efficiency was increased by increasing the current density. The amount of data collected was not sufficient to use in drawing definite conclusions.

As previously stated, there is no definite relationship between the potential of the cell and the rate at which the anode will corrode, since this potential indicates only the tendency for corrosion to take place. However, these measurements were made and recorded.

Two runs were made (Charts 2 and 3) in which the resistance was kept at a constant value and the current, in milliamperes, was plotted against time. In the first of these, a relatively high resistance of 100 ohms was used. The current, in this run, started at five milliamperes and climbed sharply to a peak, dropping off at first rapidly then more slowly. After about three and one half hours, it again began to rise and climbed steadily throughout the remainder of the run.

In the second run (Chart 3), a resistance of only one ohm was placed in the circuit and the current started off at about twenty-five milliamperes. After dropping rapidly for about three and one-half hours, it leveled off for about two and one-half hours, then continued its fall for about two hours. At the end of this time, the current began to rise and continued upward throughout the remainder of the run.

The fact that the current, at the beginning of the runs, tends to decrease, may be attributed to the increase in polarization at the cathode. Toward the latter part of the run, as the polarization reaches a constant value, the increase in surface area of the anode will cause an increase in the current.

## CONCLUSIONS

It may be concluded, from the results obtained in this experimental work, that the current efficiency of magnesium anodes, when used as cathodic protectors of steel, is generally unaffected by changes in the concentration of magnesium sulfate in the backfill. It may be further stated that the presence of manganese ion also has no effect upon the current efficiency.

The results indicate the possibility that current efficiency is appreciably affected by changes in the current density at the anode. It is suggested that further work be done in the study of this effect. It is further suggested that a wide variety of backfill conditions, for example, soils of different pH, be used in conjunction with this study.

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