

THE EFFECT OF DIFFUSIONAL PROCESSES ON THE RATE OF CORROSION.

By R. C. L. BOSWORTH, Ph.D., D.Sc., F.Inst.P.

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LIMITATIONS OF CORROSION TESTS.

Reviews of corrosion test procedure by White (1934), McKay and La Que (1937), La Que and Knapp (1945) and by others have stressed the necessity for a very close standardization of conditions. If measurements of the rate of loss of mass from a metal test piece in a given corrodant liquid are to be any guide to the behaviour of metal members under large-scale conditions, very close attention must be paid to a number of details, such as the depth of immersion, the methods of suspension or support and the conditions of aeration and circulation of the fluid ; as well as to such more obvious factors as the temperature and pH of the corrodant liquid and the presence or absence of other metals forming electro-chemical couples with the test specimen. White, indeed, has emphasized the difficulty in getting reproducible results even with different specimens of the same dimensions, and La Que and Knapp have stressed the necessity for a detailed evaluation of the proposed conditions of application in order that these may be duplicated as closely as possible in the laboratory tests.

The overall reaction of a metal dissolving in an electrolyte to give either a soluble or insoluble ionic product has long been recognized as a complicated one. Many successive physical and chemical operations are involved. Much attention has recently been given to some of these operations, especially those of a more chemical nature, such as interphase ionic transfer, anodic and cathodic polarization, and the effect thereon of inhibitors and accelerators. On the other hand the effect of the transport processes which bring the active depolarizing agent up to the seat of attack and remove therefrom the products of reaction has not received such close attention. It is clear, for example, that in the corrosion of copper by acetic acid in which the reaction is maintained by cathodic depolarization produced by dissolved oxygen, the maintenance of the chemical attack is dependent on the continuity of the supply of oxygen to the cathodic areas ; and it is conceivable that, under certain conditions, the rate of diffusion of oxygen might become a rate determining factor.

The conception of a set of physical transport phenomena entering into the final determination of the rate of chemical attack by a corrodant liquid is one which has been paralleled in recent years in other fields of applied chemistry. Thus Damköhler (1936), Edgeworth Johnstone (1939), Laupichler (1938), Hurt (1945) and Bosworth (1947) have all discussed the effect of such factors as the flow of heat and flow of reactants and resultants on the course of chemical reactions in small and large scale reactors. Further, Agar and Hoar (1948) have discussed the effect of a change of scale on an electrochemical system and have concluded that the rate controlling step for a large scale system is not necessarily the same as for a small scale system under otherwise identical chemical and physical conditions.

VARIABLES OF THE TRANSPORT PROCESS.

It appears desirable, therefore, to examine the process of corrosion with a view to enumerating and, if possible, devising methods of measuring the factors which are concerned in the transport of matter to and from the corroding surface. In this object there is one obvious mode of attack. Recently a number of authors (Sutton, 1934 ; Powell and Griffiths, 1939 ; Pasquill, 1943 ; and Boelter, Gordon and Griffin, 1946) have traced a degree of parallelism between heat loss and loss of matter by evaporation from geometrically similar bodies. Since it is not unreasonable to expect that matter loss from corroding bodies might also behave similarly, and further since the laws of conduction and convection of heat are particularly well known, the first object of this paper and of the two succeeding papers will be an attempt to trace a degree of parallelism between heat loss and matter loss by corrosion from geometrically similar bodies. This paper will be specifically concerned with transport under stagnant fluid conditions, analogous to the transport of heat in a fluid by thermal conductivity alone.

The corrosion rate q , in mass flow per unit area per unit time, and the corrosion cell e.m.f. E are, clearly, two of the properties with which we will be concerned. The quantity E is the driving force which produces a flow of matter q . While much has been discovered from purely electrochemical measurements concerning the mechanism whereby E produces the matter flow q , we are not here immediately concerned with this subject. We are, however, concerned with the property which might be defined as the overall chemical resistance (or impedance) of the system—that is to say the factor which determines the magnitude of the driving force required to produce a given flow rate. Since various successive reactions are involved in the corrosion process, this overall resistance can presumably be split into a number of series (or parallel) components, one corresponding to each step in the corrosion process ; in much the same way as the flow of heat in a multi-component system can be represented by a number of series (or parallel) thermal resistances. Among the factors contributing components to the overall chemical resistance are the transport processes leading to the removal of the anodic and cathodic products of corrosion from the immediate vicinity of the interface under attack. Removal may be effected by diffusion, turbulent diffusion, or by the convection currents set up either as a result of density changes produced by the solution of heavy metal ions, or from temperature changes. Since the mechanism of removal of the products of reaction controls the degree of polarization, it also controls the magnitude of the electric current across the metal-electrolyte interface and thus the rate of corrosion. The transport processes involved in the removal of matter from the vicinity of the interface bear a formal similarity to those exhibited by the heat loss from a hot body immersed in a fluid. Heat may be carried from such a body by molecular conduction, turbulent conduction, by forced convection if the fluid is stirred, or by natural convection.

Examples of corrosion in which an insoluble phase resulting from chemical reaction consequent to corrosion builds up a barrier to the diffusion process, or those in which the corrosion reaction is maintained by the presence of a bimetallic system providing a permanent cell e.m.f. obviously involve a transport mechanism which is more complicated than that involved in the flow of heat. However, when uniform, or general corrosion alone occurs, it would appear that the transport processes have features in common, and it is this suggested similarity which will be discussed below.

EXPERIMENTAL.

The subjects of experimentation were selected so as to avoid the more complicated types of corrosive attack. The subjects consisted of copper,

certain copper alloys and steels in acetic acid-acetic anhydride mixtures. Commercial acetic acid has a high electrical resistivity of the order 1.5×10^{-6} ohm-cms., and accordingly bimetallic corrosion is not serious. The acetates are soluble, and thus complications due to the formation of barriers are avoided. Further, experience has shown that these systems do not show the phenomenon of dezincification in which one component of an alloy selectively dissolves. The only type of corrosion is a general attack all over the surface exposed to the acid. Accordingly these systems are particularly suitable for the examination of the influence of convection on the process of corrosion.

The equipment used consisted of a cylindrical body C of the metal under test, 3 cms. in diameter and 1.8 cms. long. One flat face of this body contained a cylindrical hole 1.0 cm. in diameter and 0.8 cm. deep coaxial with the body as a whole. Into this hole there fitted snugly a second cylinder, B, of the same metal, the two top faces being coplanar. These two faces were polished together. Cylinder B was removed and weighed and then placed back in position. The air was pressed out through a hole at the back of C, and this hole was finally closed by means of a screw also of the same metal. A thin film of an acid-proof grease used for lubrication prevented the corrodant from coming into contact with any portion of B other than the front face. This equipment thus permitted a study of the attack on a definite area of a single metal face surrounded on all sides by a surface of the same metal, which thus acted as a guard ring and, by eliminating irregularities in the field of the corrodant at the edges, reduced the geometrical pattern of the flow of matter to and from the face under attack to one in a single dimension.

After subjection to the corrosive conditions for a measured time, cylinder B was removed, the acid-proof grease was dissolved in a volatile solvent and the cylinder dried and weighed.

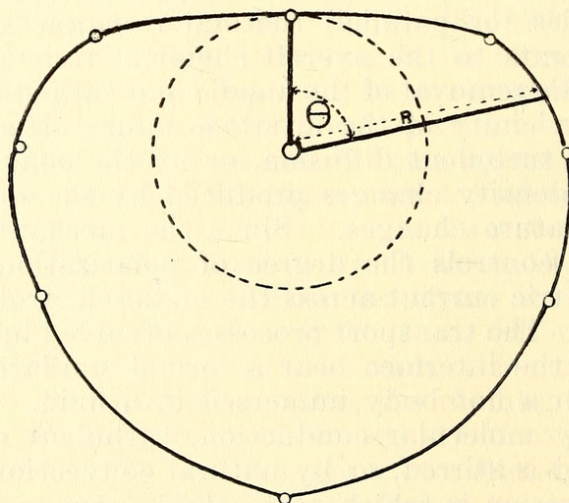


Fig. 1.

THE EFFECT OF ORIENTATION.

The equipment as described above was first used in a study of the effect of orientation on the rate of corrosion. An iron (mild steel) surface was immersed 4 cms. in a 60/40 acetic acid-acetic anhydride mixture and the rate of corrosion measured at different orientations as the face was turned in a vertical plane through 2π . The results are shown in the form of a vector diagram in Figure 1. In this diagram the r co-ordinate measures the rate of corrosion and the θ co-ordinate the azimuth.

It will be seen from the figure that the rate of loss of matter is a minimum when the corroding surface is facing upwards and a maximum when facing downwards. Evans and Mears (1934) have already remarked on the flow of heavy metal salt solution under gravity away from all surfaces except those facing vertically upwards. This flow constitutes a convection current opposite in direction, but essentially similar in nature, to the convection currents surrounding a hot body in a fluid. Thus it is seen from Figure 1 that the corrosion rate is a maximum when the convection current is most intense and a minimum when there is no convection and when the loss of matter takes place entirely by a "conductive" mechanism.

In taking measurements of the corrosion rate with all transport processes restricted to those of the "conductive" type, it is of importance to be able to estimate the error involved in any slight departure of the surface from the horizontal position—say by an angle θ . Since the top of Figure 1 is flat, it follows that the error is of the order $q/\cos \theta$ or $q(1 + \theta^2)$, where q is the measured rate. Errors of magnitude sensible in comparison with the random errors usual even in the best corrosion measurements are thus not incurred unless θ is greater than 0.2 radian or 12° , which quantity is thus a measure of the tolerance allowed on the orientation.

EFFECT OF VARYING THE DEPTH OF IMMERSION.

The property of thermal conductivity plays a large part in all successful attempts at the co-ordination of experimental determinations on the rate of conductive and convective transfer of heat. If a similar co-ordination of the effects of convection on the corrosive transfer of matter is to be attempted, it is

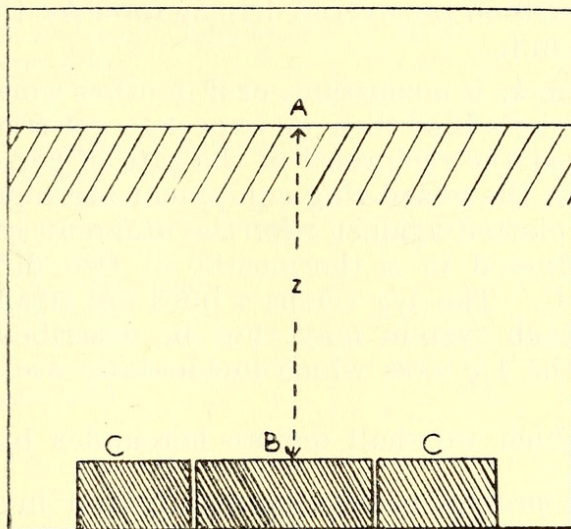


Fig. 2.

important to find that property concerned with the transport processes involved in corrosion which plays the same part as thermal conductivity does to heat flow in fluids. Such a property could be measured by an adaption of the guard-ring method of measuring thermal conductivity. If we set up the equipment, described in the section above, horizontally at a distance z below a free surface, we will effectively be concerned with one-dimensional diffusion through a distance z , the depolarizing agent (atmospheric oxygen) having to travel that distance through a stagnant layer of the corrodant liquid.

In Figure 2, let A represent the free surface of the corrodant and B and C respectively the surface under attack and the guard-ring both at a distance z from the free surface and parallel to it. We are concerned with a flow of matter

from B to the liquid ; the flow, on account of the influence of the guard-ring, being normal to the surface. This flow, the magnitude q of which may be measured by weighing the central cylinder before and after a measured time interval, is stoichiometrically connected with all chemical steps in the corrosion reaction. One of these steps is the "conductive" flow of the depolarizing agent through a distance z . The magnitude of q therefore might be expected to vary with z in the same way as the flow of heat from a geometrically similar hot plate separated from another plate, at a temperature difference θ from the former, by a convectionless thermal conductor of conductivity k_θ . In such a thermal system the heat flow q_θ per unit area per unit time is related to θ by an equation :

$$k_\theta = \frac{q_\theta z}{\theta}.$$

If dq_θ is the heat flow change associated with a change dz in the thickness of the thermal conductor, we have

$$k_\theta = \frac{1}{\theta} \frac{dz}{d(1/q_\theta)} \dots\dots\dots (1)$$

In the mass flow system involved in the corrosion process we may readily measure the change in the rate of corrosion (dq), in units of mass crossing unit area in unit time, produced by a change dz in the length of the path through which the depolarizing agent is conducted. In this system now we may define a corresponding conductivity term k_c by means of an expression analogous to equation (1), viz.

$$k_c = \frac{1}{E} \frac{dz}{d(1/q)}, \dots\dots\dots (2)$$

where by E is to be understood the overall driving force for the corrosion reaction, or the corrosion cell e.m.f.

If for a given system k_c is a constant, or if in other words the system follows a law analogous to Fourier's law, then we expect to get a straight line when the depth z is plotted against the reciprocal of the rate of corrosion ($1/q$). Experimental data obtained on the guard-ring equipment are represented in Figures 3 and 4, where $1000/q$ is plotted against z for the different systems studied. The experiments were conducted in a thermostat at two different temperatures, namely 20°C . and 70°C . The $1/q$ versus z lines are straight, but do not pass through the origin. Each system may thus be described by two constants ; the intercepts $1/q_0$ on the $1/q$ axes which incidentally are always positive, and

the slopes $\left(\frac{dz}{d(1/q)} \right)$, which we shall denote hereunder by the symbol j . We

see, therefore, that the process of transport of matter involved in a corrosion reaction taking place under "conductive" conditions involves two properties of the system, j and q_0 . The significance of these properties will be discussed below, but first it is desirable to consider the units in which these quantities are to be measured and the magnitude of these properties for typical systems.

UNITS.

Many problems connected with the transport of matter and of heat which are too complicated for a complete mathematical treatment have been successfully treated by the use of dimensionless quantities. In order to combine the quantities connected with the transport phenomena concerned with corrosion, it is first necessary to use a consistent set of units throughout. The various phenomena involved can be reduced to four fundamental dimensions. Now q the rate of corrosion is, in the technical literature, commonly measured in units

of milligrammes decimetres⁻² days⁻¹, while E , the corrosion cell e.m.f., is commonly measured in volts. We shall accordingly take for our four fundamental units the quantities, decimetres, milligrammes, days and volts. Thus the quantity j above is to be measured in milligrammes decimetres⁻¹ days⁻¹, while k_c is to be measured in milligrammes decimetres⁻¹ days⁻¹ volts⁻¹.

The units in which the other properties of importance are to be measured will be given later. For convenience this system of units will be referred to as the d.m.d.v. system.

RESULTS.

The experimental results calculated from the lines shown in Figures 3 and 4 are tabulated in Table 1. For each system and temperature studied the two properties j and q_0 are recorded, each of course, in d.m.d.v. units.

TABLE 1.

Metal.	Corrodant.	Temperature.	Slope j Milligrammes dm ⁻¹ , day ⁻¹ .	Reciprocal Intercept q_0 Milligrammes dm ⁻² , day ⁻¹ .
Copper.	Acetic anhydride	20° C.	9.6	51
"	60/40 acetic acid/acetic anhydride	"	10.5	125
"	Glacial acetic acid	"	13.8	150
"	50% aqueous acetic acid ..	"	6.0	97
"	50/50 acetic acid/benzene ..	"	195	405
"	60/40 acetic acid/acetic anhydride	70° C.	190	2000
"	Glacial acetic acid	"	710	2000
Brass.	Acetic anhydride	20° C.	1.6	71
"	60/40 acetic acid/acetic anhydride	"	6.2	66
"	50% aqueous acetic acid. ..	"	3.3	70
Phosphor bronze.	60/40 acetic acid/acetic anhydride	20° C.	18.2	135
"	Glacial acetic acid	"	20.0	130
"	50% aqueous acetic acid ..	"	16.0	100
"	Glacial acetic acid	70° C.	660	1050
Mild steel.	60/40 acetic acid/acetic anhydride	20° C.	52.0	1000
"	Glacial acetic acid	"	62.0	950

DISCUSSION.

The lines represented on Figures 3 and 4 relating the variation of the rate of corrosion with the depth can be put in the form

$$\frac{1}{q} = \frac{1}{q_0} + \frac{z}{j} \dots\dots\dots (3)$$

A similar expression would have been given for the heat loss across a thermal conductor of various thickness from a hot body, which however is not bare but thermally lagged so that the rate of heat loss can never exceed a certain figure.

The property j is related to the correction conductivity k_c by the expression

$$j = Ek_c \dots\dots\dots (4)$$

and is more convenient than k_c because the quantity E is not directly concerned in corrosion measurements. The quantity j is a measure of the conductivity of the corrodant for the depolarizing agent and is thus a measure of a sensitivity of

the reaction concerned to control through limiting the supply of depolarizing agent. A reaction giving a small j such as brass in acetic anhydride is strongly dependant on the supply of atmospheric oxygen.

The quantity q_0 is a measure of the rate of corrosion when the depolarizing agent is made instantly available at the surface and is thus a quantity of more direct chemical significance than measures of q under any standard conditions of

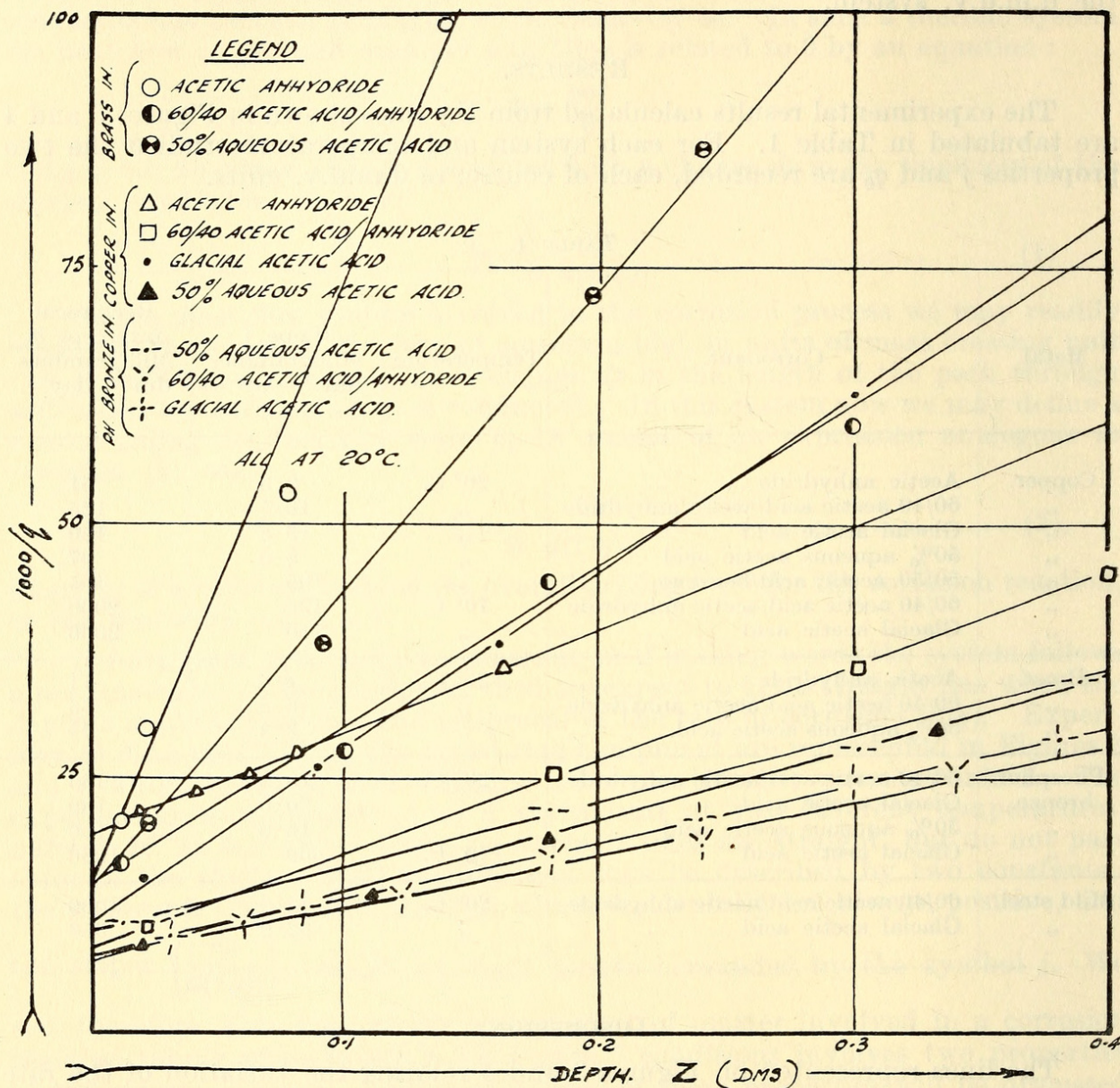


Fig. 3.

immersion or aeration. The ratio E/q_0 is a measure of the resistive force opposing the corrosion process when the effect of all physical factors limiting the supply of the depolarizing agent to the surface have been eliminated. If we denote this resistance by r , viz.

$$r = E/q_0 \dots \dots \dots (5)$$

We then have, for the net driving force available for maintaining the transport of depolarizing agent to the surface under attack when the specimen is corroding at a rate q ,

$$E - qr \text{ or } E(1 - q/q_0) \text{ volts.}$$

This is the factor with which we will be concerned in treating the more complicated phenomena concerned with transport processes involving forced and natural convection.

SUMMARY.

The influence of the processes involving the transport of matter on the rate of corrosion has been studied by means of a circular disc protected by a guard-ring. This device reduced the geometrical nature of the flow of matter to one in a single dimension. The variation of the corrosion rate of such a surface was

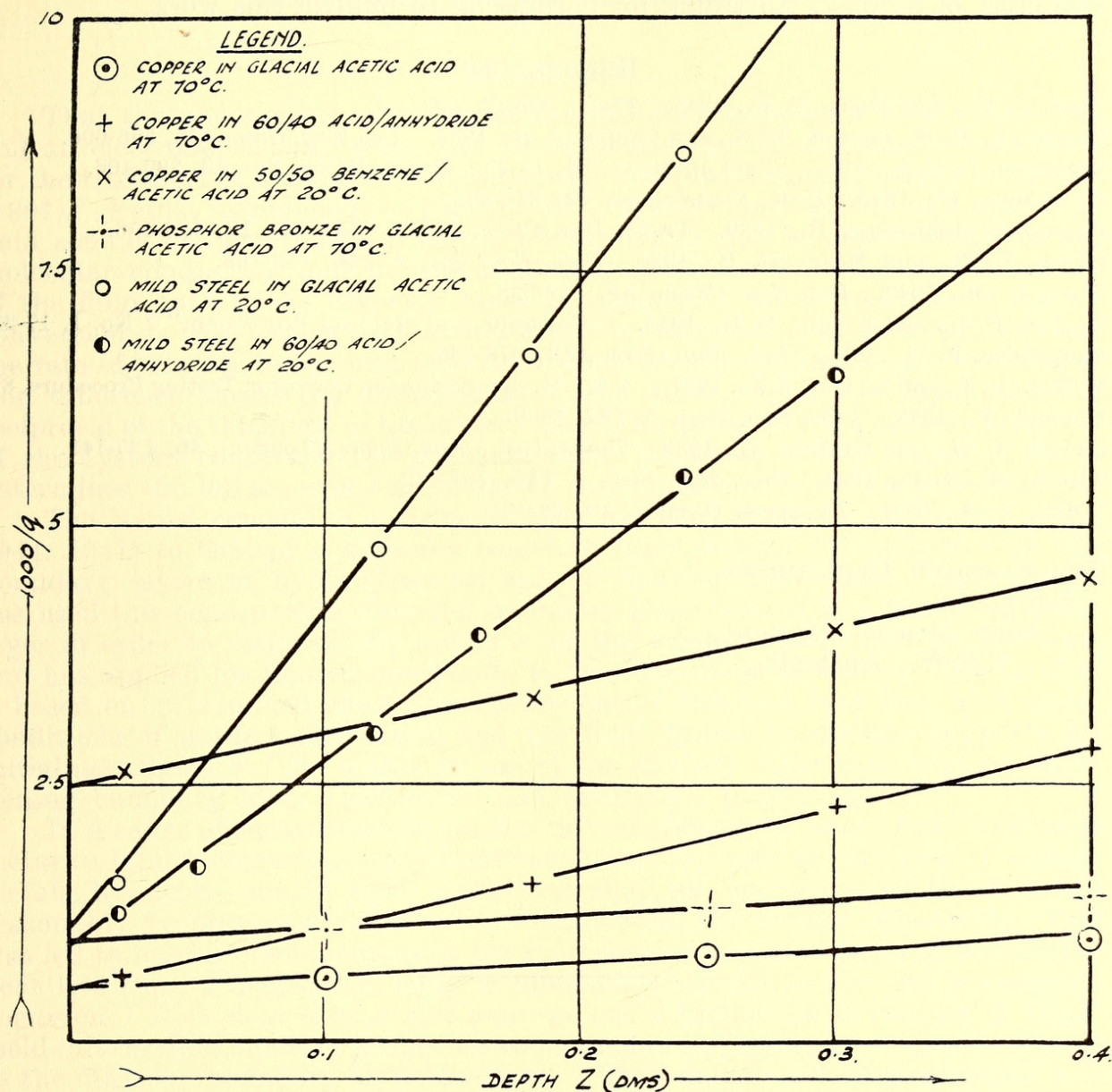


Fig. 4.

studied as a function of the orientation of the surface and shown to be a minimum when it faced upwards. It was concluded that convective transfer was absent under these conditions. The corrosion rate, from a horizontal surface facing upwards and protected by an electro-chemical guard-ring, was then studied as a function of the depth of immersion.

The systems studied included copper, copper alloys and steel in acetic acid, acetic anhydride mixtures. Experimental results plotted in the form : reciprocal

of the corrosion rate ($1/q$) versus the depth (z) of immersion give straight lines with positive intercepts on the $1/q$ axis. These intercepts have been interpreted as a measure of the rate of corrosion under such conditions that the depolarizing agent (atmospheric oxygen) is made freely available at the surface. The slopes have been interpreted as a measure of the "conductivity" of the corrodant for the depolarizing agent, a factor which, it is suggested, would be of primary importance in the interpretation of the effect of convection of the rate of corrosion.

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The Research Department,
C.S.R. Co.,
John Street, Pyrmont,
N.S.W., Australia.



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