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FUNDAMENTAL FACTORS IN CORROSION.

with a Supplement,

NOTES ON THE PLATING OF CHROMIUM ON STEEL.

A THESIS

By

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FUNDAMENTAL FACTORS IN CORROSION.

By

George M. Enos.

Introduction.

The corrosion of metals and alloys is by far one of the most serious problems in the field of applied chemistry and metallurgy. Not only is the problem one of the greatest practical importance, but the theoretical aspects are as yet far from being thoroughly understood. Yet so great is the mass of literature published that a historical review of only the general aspects of the subject would be a treatise in itself. No attempt can be made in this paper to review all of the literature, but a classified, selected bibliography is appended which covers many of the theoretical and practical aspects of the subject.

Metals and alloys that are generally resistant to the attack of corrosive media are few in number. Of these, the noble metals and some of their alloys are probably the best known and least attacked by the atmosphere and other corrosive agencies. Of the more abundant and cheaper metals and alloys, many have been studied and tested for their resistance to corrosion, but this field is so broad that there

are still innumerable problems to be solved. For resistance to certain specific corrosive media, various metals and alloys have been developed which serve their purpose quite well. However, much of the developement work has been done on purely an empirical basis, and the old reliable cut-and-try methods have been much employed.

It is the purpose of this investigation to study the theories of corrosion and the factors affecting corrosion rates, particularly as the factors may affect corrosion in its early stages. The method of investigation has been to study the literature, and as far as possible to do experimental work on points on which the recorded data is not clear or is conflicting, or on which no work has been done.

No defense is needed for intelligent research on corrosion problems. According to the best authorities [41]a

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(a) Numbers refer to the appended bibliography.

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the annual loss through the rusting of iron and steel alone amounts to many millions of dollars, and the loss through corrosion of other metals and alloys is also large. Before attempting research and testing work in any field of corrosion investigation it is essential to have a working knowledge of the theories and factors involved, insofar as they are known at the present time.

Perhaps the best definition of corrosion so far advanced is that of Rosenhain[6] who states that corrosion is

> The strong tendency for all metals when in contact with the agents of nature, viz, oxygen, water, and carbon dioxide, to revert to their condition of more chemically stable equilibrium.

It is obvious that in a broad sense corrosion is the oxidation of metals and alloys, for the products of corrosion are usually the same as a possible natural source of the metal. Thus when iron rusts, it forms a hydrated ferrous-ferric oxide, similar in many respects to some iron ores and if dehydrated, rust certainly becomes oxide of iron. In short, the products of corrosion are products of oxidation, and are either salts, oxides, or hydroxides of the metal, or are mixtures of these. The process is one of oxidation of the metal, since the change of valence indicated in any chemical equation expressing a corrosion reaction will indicate the loss of one or more electrons by the corroded metal. If the term corrosion be made broad enough to include all cases of the failure of engineering metallic materials as the result of chemical reactions, then our definition of corrosion should rather be in terms of the failure (or/tendency towards failure). It is sufficient, however, as will be shown later, to consider corrosion as a process of oxidation, if we define oxidation as "any process that results in valence becoming more positive or less negative" (Deming - General Chemistry).

During the many years that corrosion has been studied, various "theories" have been advanced to explain the mech-

anism of the phenomonon, and of all these theories, the electrolytic, acid, and direct oxidation theories have received the widest acceptance. No one of these theories explainsclearly the mechanism of the corrosion initiation, although several of them serve to explain the reactions in corrosion, after the process is started. Apparently, the reason why so many different theories have been suggested is that the various factors which affect corrosion processes give appearances of differences under divers conditions.

Preliminary to presentation of the results of the present investigation it may be of general interest to pass in review the several theories of corrosion, to critically examine these, and to select the explanations of the phenomena of corrosion which will best serve in making clear the inception and progress of the corrosive attack.

There are several theories of corrosion which have been advanced, and of these, there are seven which have been more or less advocated. R. J. Anderson and the writer (64) have abstracted these and the statement of these theories here is essentially the same as published elsewhere.

SIMPLE OXIDE THEORY.

This theory assumes that a metal is attacked chemically by oxygen or other gas without having previously passed into solution. Many investigators have believed this theory to be sufficient explanation for most corrosion processes, but the supporters of the electrolytic and acid

theories have advanced evidence that liquid water, in addition to oxygen, is essential to the corrosive attack. The position taken by Bengough (15, 13), that some cases of corrosion can be explained on the basis of direct oxidation seems plausible. If iron is corroded in atmospheric air, the simple oxide theory postulates direct union of the iron and oxygen atoms. This conception is frequently regarded as the same as the oxidation of metals when heated in dry air or oxygen.

Bengough and Stuart (15) have aptly pointed out that chemical reactions require contact between the chemical reacting substances and that part of the energy of the system is liberated in the form of heat, whereas electrochemical reactions are characterized by the liberation of the energy of the system as electrical energy, and also by the conditions that the reacting substances must be capable of ionization, and must be spatially separated.

ACID THEORY.

Although originally stated by Calvert (18) the acid theory of corrosion has been developed and supported by others, including Friend (2, 3). This theory postulates that acid, oxygen, and water must be present before corrosion takes place. The acid may be as weak as carbonic acid. The reactions of iron with this acid would be expressed as follows:-

(1) $Fe + 2\ CO_2 + 2\ H_2O = FeH_2(CO_3)_2 + 2\ H$ (soluble ferrous bi-carbonate)

(2) $FeH_2(CO_3)_2 + Aq. = FeOAq. + H_2O + CO_2.$

(3) $4\ FeOAq. + O_2 = 2\ Fe_2O_3Aq.$ (rust).

The nascent hydrogen liberated in the first reaction combines with dissolved oxygen to form water. Carbon dioxide is liberated by the decomposition of ferrous bicarbonate in the presence of water, and is free to attack more iron. Thus the process is cyclical and a small amount of acid can assist in oxidizing an indefinite amount of iron.

Friend, Armstrong, Moody[19] and others have ably supported this theory, but it is difficult to see the distinction between this theory and the electrolytic theory, except that this theory is not usually expressed in terms of ionic reactions.

ELECTROLYTIC THEORY.

According to the advocates of this theory, corrosion is electrochemical in nature. Water is an electrolyte, and ionizes, though to a small extent, to hydrogen and hydroxyl ions. Therefore, it is not necessary that an acid be present before corrosion can proceed. If a metal such as iron, be placed in water, or if the conditions be such that a film of water is on the metal, there is a strong tendency for the metal to dissolve in the water. Or, in other words, the metal tends to pass from the metallic (atomic) state to the ionic state. When this change of state occurs, the atom of the metal assumes a positive charge of electricity, and consequently the metal mass which it leaves is charged negatively. The tendency for a metal to dissolve in an electrolyte is called its solution pressure, hence corrosion is dependent

upon the solution pressure. The reaction is expressed:-

$$Fe + 2\,H^{+}OH^{-} \longrightarrow Fe^{++}(OH)_2^{-} + H_2.$$

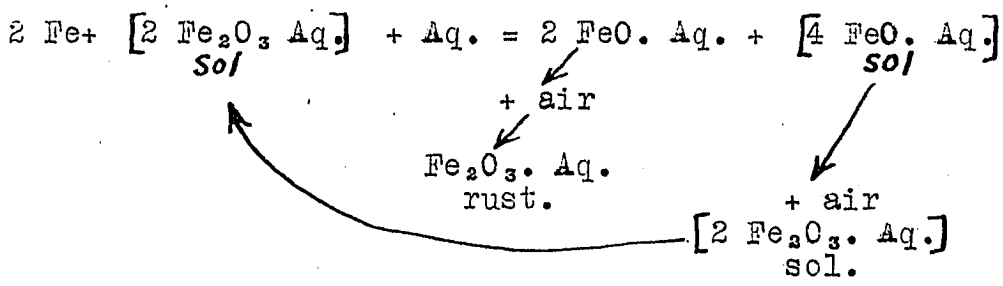
It has been shown by Sammis, as well as by the work of Kahlenberg[31], that certain types of chemical reactions that take place in aqueous solutions which conduct electricity can be duplicated in non-conducting liquids. The fact that corrosion of metals can take place in non-electrolyte, as has been shown by Gates[24], is proof that an electrolyte, is not required for corrosion. The theory as advanced by Whitney[20] has been termed electrolytic in contrast with the acid theory, implying that the latter is not electrolytic in nature. Of course, both theories are to be interpreted from the electrochemical point of view. Bancroft[25] has recently discussed the electrolytic theory of corrosion at considerable length and the reader is referred to his paper for an extended discussion of this theory.

AUTO-COLLOIDAL CATALYTIC THEORY.

According to Friend[26, 27, 3] the rusting of iron in the presence of liquid water and air or oxygen is a catalytic process, in which iron hydroxide hydrosol, produced under suitable conditions acts as a catalytic agent in continuing the process. This theory is valuable in that it calls attention to the effect of colloids in corrosion processes.

The theory postulates corrosion as a process by which the colloidal ferrous hydroxide, formed as the first

step in the cycle, flocculates by contact with air to hydrated ferric hydroxide. The hydrated ferric hydroxide is reduced by contact with iron, and then oxidized by contact with air. In this manner the rusting continues. The iron, when it first comes in contact with liquid water, is oxidized by air (or oxygen) to colloidal ferrous hydroxide. In this colloidal condition it is apt to be particularly reactive chemically, and is easily oxidized to the ferric hydrosol. When the sol flocculates or precipitates out, the product is rust. The schematic representation of this theory is as follows:-



On the basis of this theory, it is evident that Friend has modified his earlier views (support of the acid theory) or at least considers another factor in the corrosion of iron as important. It has been pointed out very aptly by Hughes[28] that while the establishment of a colloidal substance as a product of a corrosion process will help in understanding certain anomalous facts concerning corrosion yet this does not give any better comprehension of the fundamental cause.

HYDROGEN PEROXIDE THEORY.

Dunstan[29] and his co-workers have shown that hydrogen-peroxide is an intermediate product in the corrosion of

some metals, including copper, lead, and zinc. Apparently it is not formed in the corrosion of iron. If it were formed, the reactions given below would be expected:-

$$Fe + O_2 + H_2O = FeO + H_2O_2$$

$$2\ FeO + H_2O_2 = Fe_2O_3\ (OH)_2,\ (Fe_2O_3 \cdot H_2O),$$

and the excess of the hydrogen peroxide reacting with the iron

$$Fe + H_2O_2 = FeO + H_2O, \text{ and}$$

$$2\ FeO + H_2O_2 = Fe_2O_2\ (OH)_2,\ (Fe_2O_3 \cdot H_2O).$$

The knowledge that hydrogen peroxide is an intermediate product in the oxidation of some metals by air and water may be of some value, but it can hardly be postulated that hydrogen peroxide is a necessary accompaniment of the process, either at the start, or during the progress of the corrosive attack.

ADSORPTION THEORY.

It has been pointed out by Saklatwalla[30] that the adsorption of gases may have a very marked effect upon the nature and rate of corrosion. When a gas is condensed as a film upon the surface of a solid body, it seems probable that such adsorption would have a tendency to impart surface activities to the body, dependent upon the degree of adsorption. If there is a definite relationship between the adsorption of the gas, and the corrosion of the metal by the gas then the rate of corrosion depends, among other things, upon the density of the film. If the metal has a high degree of adsorption, the condensation would be high, the

velocity of the reaction would be high and surface oxidation would take place quickly. It is suggested that high interacting velocity resulting in a quick production of a protective film on the surface of the metal is an essential factor in producing non-corridibility in the case of attack by corrosive gases. To sum up, it is alleged that certain metals are non-corridible because they produce adsorbed surface gas films of high concentration, because the metal is capable of adsorbing large amounts of the attacking gas.

It would seem that since direct experimental evidenve is not presented, that the hypothesis while of some value, leads to the inference that the inception of corrosion in the case of corrosion of metals by gases is the result of direct oxidation.

BIOLOGICAL THEORY.

It has been suggested that lowly forms of life enter into the reactions which occur when iron corrodes. Probably the secretions of animal and vegetal organisms increase the corrosion of metals, where these secretions come in contact, directly or indirectly with the metal. Since corrosion takes place readily in the absence of living matter, corrosion is not prevented, though in some cases it might be retarded, by excluding such matter. This aspect of the problem should not be overlooked, but it probably is not of major significance.

SUMMARY OF THE THEORIES.

In considering the theories advanced it will be noticed

that no one is definite in describing the mechanism of corrosion inception, nor is any one theory sufficient to explain all observed cases of corrosion.

Naturally, enthusiastic supporters of the more important theories have endeavored to prove that the theory advocated is exclusively correct. Many of the experienced investigators, such as Bengough, have taken the view point that corrosion may be either chemical or electrochemical, and that all corrosion may be explained by one or the other of these two reactions. There seems to be no good reason why the acid theory cannot be interpreted in terms of the electrochemical theory, and the other theories may be explained either in terms of direct oxidation or in terms of the electrochemical reactions, or else are untenable.

It has been suggested that electrochemical and chemical reactions are identical. Desch and Whyte[37, 38] suggest that there is no essential difference between electrically stimulated and natural (chemical) corrosion. This view is shared by the writer. It seems certain that chemical corrosion and electrochemical corrosion are the same qualitatively but not necessarily quantitatively.

APPLICATION OF THE MODERN CONCEPTION OF MATTER TO CORROSION.

None of the theories discussed serve to explain the inception of corrosion, in definite terms. It seems that an explanation of the initiation and progress of corrosion might

well be given in terms of the modern conception of the constitution of matter, and so far as the writer is aware this has not been done. In the following paragraphs it is the purpose of the writer to develop the theory of corrosion inception and progress in terms of the electron theory of matter. No doubt most investigators are thoroughly conversant with this general theory, but its application to the problem of corrosion seems to have been overlooked, or at least deemed of little interest.

The electronic theory of the constitution of the atom has been developed as a workable tool in the fields of chemistry and physics through the investigations of Soddy, Rutherford, Lewis, Thomson, Langmuir, Harkins, Mosely, Milliken, Aston, Bohr, and many others. It is beyond the scope of this paper to review the theory in general or the many variations that have been suggested. It is now generally agreed that all of the atoms of matter possess the same general type of structure. The atom consists essentially of a minute nucleus surrounded by a system of negative electrons. The nucleus is presumed to contain practically all of the mass and all of the positive electricity of the atom. The electron has the smallest mass of any known particle of matter. The most stable arrangement of electrons is that of the pair in the helium atom, and the next most stable arrangement is the octet i.e. a group of eight. The electrons are arranged in shells, and it is generally

agreed that the outer most ring of electrons contains those which give the property of valence to the atom. Thus the force exerted by the atom and consequently its physical and chemical properties will depend upon the configuration assumed by the planetary electrons.

It is necessary, if the atom is to be neutral, that the number of positive electrons in the nucleus be equal to the number of planetary electrons, and the addition of negative electrons or their withdrawal constitutes chemical change. Thus the loss of two negative electrons from an iron atom converts it into a ferrous salt, and the loss of three electrons converts it into a ferric salt. Chemical action may be properly regarded as starting by the gain or loss of negative electrons or by the transference or shifting of negative electrons by different atoms.

Any atom which is not electrically neutral is termed an ion, and this may have either a negative or a positive charge. Thus, in an ion, the number of positive electrons can in no case be equal to the number of negative electrons, and the charge of an ion whether positive or negative depends on whether the neutral atom lost or gain negative electrons. The ionization of the iron atom is represented by $Fe^{\circ} - 2\,e \longrightarrow Fe^{++}$ that is, the loss of two electrons has disrupted the electrical neutrality so that the ionized iron atom possesses an excess of two positive electrons on the nucleus.

Since the arrangement of the electrons about a nucleus and their number determines the physical and chemical properties of elements, the relative corrosion of metals and alloys under given conditions must be explainable only in terms of the loss, gain, transference or sharing of the electrons by the metal or alloy so corroded. When atoms of elements combine to form a molecule, they may gain or lose electrons, or else hold some of their outer electrons in common. If the arrangement of the electrons in the outer shell of an atom is such that certain electrons (primary valence electrons) are readily lost or transferred, then a more stable configuration results from such loss or transference. In the same way, the arrangement may be such that a more stable configuration results from the addition of electrons. It is this tendency to gain or lose electrons that determines the stability of an element. The statement made that corrosion is the tendency for metals to pass to a condition of more stable equilibrium means simply its tendency to gain or lose electrons.

It may now be postulated that all corrosion starts by the loss or transference of electrons from the metal corroded and the gain or transference of electrons to an atom of the molecule of the corroding medium - that is, the metal is oxidized. Corrosion must be regarded as a chemical change (obviously a physical one also), and on the basis of the electronic theory of matter chemical change is the result of the

addition of negative electrons to the outer planetary ring or their withdrawal from that shell. The application of the electronic theory of the constitution of the atom to practical corrosion problems is susceptible of very great developement, but this has not been done in the investigation reported here.

Ionization in its simplest case means the detachment of an electron from a neutral atom. The number of electrons which an atom can gain or lose depends upon the nature of that atom; the number it can gain is equal to the number of electrons in the outer layer, and varies from one to eight, according as the element belongs to one or another of the Mendeleefian groups; the number it can lose (receive) is eight minus the number in the outer layer. The molecule of a chemical compound is regarded as made up of atoms, some of which have lost electrons, while others have gained them, so that the former are positively, and the latter negatively, electrified, the forces between the electrical charges on the atoms and electrons binding the atoms together in such a way as to form a stable system.

For a bi-valent metal, the inception of corrosion is expressed by the form $\text{Metal}^{\circ} - 2\,e \rightarrow \text{Metal}^{++}$. This, or an equivalent expression, indicates the mechanism of all corrosion inception, irrespective of the metal and irrespective of the corroding medium. The loss of two electrons from the iron atom converts the iron atom into a ferrous

salt, while the loss of three electrons converts it into a ferric salt. The inception and progression of corrosion may be represented as follows:

$$M^\circ - 2\,e \rightarrow M^{++}$$

$$X + 2\,e \rightarrow X^{--}, \text{ and}$$

$$M^{++} + X^{--} \rightarrow M^{++}\,X^{--},$$

where M is any metal and X is corroding medium, Or, taking a case where M is a metal and AB is an aqueous corroding solution,

$$M^\circ + A^+B^- \longrightarrow M^+B^- + A^\circ,$$

that is, prior to immersion the M atoms are electrically neutral, but upon immersion M loses one or more electrons because of the driving force of solution pressure (tendency to lose or exchange electrons under specific conditions), and it thus becomes positively charged. The solution AB is ionized when A gives up electrons to B, and the negative electrons from M attach to A^+ ions and A becomes neutral, the salt MB being formed.

In the oxidation of metallic copper, the fundamental assumption of the electronic theory calls for

$$Cu^\circ - 2\,e \rightarrow Cu^{++}.$$

In sulphuric acid (hot concentrated),

$$Cu^\circ + 2\,H_2{}^{++}SO_4{}^{--} = Cu^{++}SO_4{}^{--} + SO_2 + 2\,H_2O.$$

In dry hot oxygen,

$$2\,Cu^\circ + O_2 \overset{+\,-}{\longrightarrow} 2\,Cu^{++}O^{--}.$$

Taking the oxidation of iron;

$$Fe^{\circ} - 2\ e \rightarrow Fe^{++}.$$

In hydrochloric acid,

$$Fe^{\circ} + 2\ H^{+}Cl^{-} \rightarrow Fe^{++}Cl_2^{-} + H_2.$$

In copper sulphate,

$$Fe^{\circ} + Cu^{++}SO_4^{--} \rightarrow Fe^{++}SO_4^{--} + Cu.$$

In water,

$$Fe^{\circ} + 2\ H^{+}OH^{-} \rightarrow Fe^{++}\ (OH^{-})_2 + H_2.$$

In sulphuric acid,

$$Fe^{\circ} + H_2^{++}SO_4^{--} \rightarrow Fe^{++}SO_4^{--} + H_2.$$

It should be emphasized that when atoms combine to form molecules they usually hold some of their outer electrons in common, two electrons being thus held for each chemical bond. Thus, one atom lends or transfers electrons to the other so as to fill up the outer layer of the first or vice versa, - that is, the atoms share their electrons for the purpose of combination, and the electrons which are held in common tend to hold the two atoms together.

On the basis that all chemical reactions start by release or gain of electrons by one of the reacting substances, corrosion inception can be very readily explained by the electronic theory. After the initiation of the action, then ensuing reactions might be termed chemical or electrochemical as the process proceeds to completion, in terms of the older chemistry, depending upon whether the energy of the reacting system is liberated as heat (chemical reaction) or as elec-

tricity (electrochemical reaction). Such designation is, however, quite superfluous since electron interchange is the accompaniment, or better the cause, of the continuation of the reaction. The value of the electronic conception of corrosion lies in the fact that it not only explains the inception of corrosion - that is, the initiation of chemical change - but it can also be applied to explanation of the mechanism of the process from the initial stage to completion. This may be contrasted with the various "theories" of corrosion which attempt to explain the mechanism of corrosion processes after the initial stage and in terms of the older chemistry. Since there are so many variable factors in any corrosion process, it is evident that under different conditions the details of the mechanism of the process will also be different. Thus, descriptions of the most common variations in the mechanism or process of corrosion after inception have been designated as theories of corrosion. The present work shows that all of the theories which have been advanced simply attempt to describe variations in the mechanism of corrosion after the initial reaction - that is, loss of electrons, has started.

Thus, taking the case of the simple oxide (direct oxidation) theory which assumes direct interaction of atoms: All chemical reactions are electronic in nature, and simple oxidation is readily explained as the continuation of a process which is initiated by electron loss. At high temperatures,

iron and oxygen interact directly, and this has been regarded as a case of corrosion since it is one of oxidation. The inception of the oxidation of iron is expressed as follows -

$$Fe^{\circ} - 2\,e \rightarrow Fe^{++},$$

and the ensuing oxidation - that is, the mechanism of the process as explained by the direct-oxidation conception, is represented by

$$2\,Fe^{\circ} + O_2 \overset{\pm\mp}{\longrightarrow} 2\,FeO$$

Ferrous oxide is an intermediate stage in a series of reactions, whose products are ferric oxide, Fe_2O_3, and finally magnetic oxide of iron, Fe_3O_4, by further oxidation.

Taking next the case of the acid theory of corrosion, which assumes that an acid must be present in addition to water and oxygen for the process to proceed; the inception of oxidation is the same as before, namely -

$$Fe^{\circ} - 2\,e \rightarrow Fe^{++},$$

and the ensuing reaction with carbonic acid - that is, the mechanism of the process as explained by the acid theory, is represented by

$$Fe^{\circ} + H_2^{+\mp}CO_2^{--} \longrightarrow Fe^{++}CO_2^{--} + H_2.$$

Ferrous carbonate is an intermediate product in a series of reactions, the final product being say ferric hydroxide. The acid theory simply serves to explain the mechanism of corrosion reactions in the presence of an acid, but it does not explain the inception of corrosion. By the interaction of iron and carbonic acid, iron first loses two electrons and is oxidized to ferrous carbonate.

Referring to the electrolytic or electrochemical theory, this assumes passage of a metal, when in water, to the ionic state with subsequent oxidation. It is evident that the electrolytic theory simply serves to explain the mechanism of corrosion, after its inception, under electrochemical conditions - that is, the corroding medium must be an electrolyte. The inception of corrosion under these conditions is the same as before - that is,

$$Fe^{\circ} - 2\,e \longrightarrow Fe^{++},$$

and in an electrolyte like water, the reaction proceeds according to

$$Fe^{\circ} + 2\,H^{+}OH^{-} \longrightarrow Fe^{++}\,(OH^{-})_2 + H_2.$$

Ferrous hydroxide is an intermediate product in a series of reactions which finally yields ferric hydroxide. According to the electronic conception, iron first loses two electrons when in contact with the electrolyte water and must lose three electrons to be oxidized to the ferric state.

In the case of the auto-colloidal catalytic theory postulated by Friend, the inception of corrosion is the same as before. In water, the iron first loses two electrons, and "the formation of colloidal ferrous hydroxide" implies the oxidation of iron to the ferrous state. The formation of the ferrous hydroxide hydrosol is preceded by electron loss from the iron, and the auto-colloidal catalytic theory like the others simply serves to explain the mechanism of corrosion under a specific set of conditions.

With regard to the hydrogen-peroxide theory, this indicates that hydrogen peroxide is simply an accompaniment of the oxidation of iron to the ferrous state, and this oxidation must necessarily be preceded by the loss of electrons from the metal. While hydrogen peroxide is not actually formed during the corrosion of iron by waters, it is formed during the corrosion of zinc, but this is simply incidental.

In the case of the adsorption theory, the initiation of corrosion attack - that is, oxidation, is ascribed to high interacting velocity of a gas owing to a high degree of adsorption of that gas, but this conception simply described an accelerating condition of reaction. If a surface film which is protective be formed by gas attack, such a film must be the result of initial electron loss.

The biological theory simply states that corrosion may be accelerated owing to the action of organisms, and is not tenable if enlarged to assume actual feeding on metal by organisms.

The electronic conception of corrosion iniation has the further advantage that it will explain cases of corrosion of metals in non-electrolytes, and also in cases where corrosion is of a different nature than is ordinarily encountered. For example, in the failure of steel by the exposure to nitrogen or hydrogen at high temperature and pressure.

The various theories advanced are but descriptions of the roads by which, and the manner in which corrosion

progresses. Before any corrosion can occur there must be an initiating cause or tendency, and this tendency is common to all forms of corrosion attack. It seems probable that the electrochemical (electrolytic) theory serves to explain the mechanism of the progress of corrosion, once it is started, in more cases than any other one hypothesis.

To sum up: The writer postulates corrosion (oxidation) as being initiated by the loss of electrons from metal atoms, whereby the metal is oxidized. Electrons are detached by electrical forces which are sufficient to dislodge one or more electrons from an atom. The further progress of corrosion may be described in terms of the "theory" which suits the particular conditions involved, but it should be remembered that the shifting of electrons must be a necessary accompaniment of the progress of the corrosion.

FACTORS INVOLVED IN CORROSION PROCESSES.

While corrosion (chemical change) is the result of electron loss or transference between the atoms of metals and those of the corroding medium, it should not be overlooked that many factors influence the process and determine the speed of the complete reaction. It is one of the primary purposes of this investigation to study these various factors, and their influence, particularly during the initial stages of the corrosion process.

The corrosion of metals and alloys may occur in liquids, in gases, or in solids and in special variations of these media. Thus in the case of a liquid it may be acid,

alkaline or neutral, and the solution may be dilute or concentrated. If the corroding medium be a gas it may be either dry or moist, and the temperature variations may be great. More over, the gas may be oxidizing, as ordinary air, or reducing, or neutral. The metal may be alternately exposed to a liquid and to a gas, as for example, exposed alternately to sea water and to the air. Probably corrosion in solids, referring particularly to corrosion in the earth, can best be considered as corrosion in a liquid under special conditions. There are many factors affecting the nature and rate of corrosion in any medium. Some of the most common of these factors are

1. Chemical composition of the metal or alloy.
2. Physical condition of the metal or alloy.
3. Chemical composition and concentration of the corroding medium.
4. Velocity of the corroding medium, or the velocity of the metal in the medium.
5. Temperature of the medium.
6. Time period of exposure.
7. Solution pressure of the metal or alloy, which depends upon (1), (2) and (3), and is a measure of the tendency towards electron transference.
8. Films and coatings, whose formation is dependent upon the rest of the factors.
9. Electrical conditions of immersion.

10. Effect of light.

Study of these factors should throw light on many corrosion processes, and it should be emphasized that for testing purposes at least it is possible to hold all of the factors constant within limits and examine the effects of variations in them. Any additional factors which may at first seem in evidence can usually be classified as part of one of those mentioned above.

The resistance of different metals and alloys to corrosion under the same conditions may be, and usually is very variable. Thus, the corrosion of an alloy may be very rapid in an acid-gas atmosphere but very slow in sea water or in the ordinary air. The usual types of corrosion met with in metals and alloys are included under the following: (1) corrosion from ordinary atmospheric effects; (2) corrosion from special atmospheric effects, for example, in manufacturing centers where the air is less pure; (3) corrosion in special media, such as gases, or acids and other corroding liquids; and (4) corrosion by heating effects.

There is close analogy between corrosion in solution and corrosion in gases and vapors - that is, in the corrosion process after inception. The effects of the various factors upon the corrosion of certain metals and alloys has been examined for several sets of conditions and the data and discussion follows. It has not been possible to make laboratory

experiments to determine the effects of every one of the factors. In each case the literature, has been freely consulted and conclusions drawn.

CORROSION AND THE RATE OF CORROSION.

Before proceeding with the discussion of the various factors, it is necessary to distinguish carefully between what is meant by corrosion and corrosion rate. If any change of physical state involving oxidation of the metal has occurred, then some corrosion has taken place. This change in state may be of extremely small magnitude and not easily detected. To express the corrosion of a metal means more than expressing loss in weight, through the change of state, and, usually, a removal of all or a part of the corrosion product from the metal. The actual corrosion is best expressed as a summation of the effects of all the factors involved. These effects may be shown in a variety of ways, as for example, the formation of salts, oxides, or hydroxides; by the deposition of metals, salts, oxides or hydroxides; by the physical state of these products and depositions; by the formation of coatings which may accelerate, or retard the corrosion rate, or have no effect; by the formation of pits; by embrittlement; by passivity; by selective corrosion; by disintegration; and possibly other less common effects.

The corrosion rate involves the idea of the extent or amount of failure per given time unit. For convenience, and since no other method of comparison is readily available,

the corrosion rates are usually given as loss in weight per unit area of exposed surface, per unit time.

Whether a metal corrodes or not is one phase of the problem. If it does corrode two things must be considered. The rate of corrosion, and the nature of corrosion - that is, the summation of the effects of the various factors involved.

In the following pages the nature of corrosion will be given in the discussion, and if necessary in the tables, and the corrosion rate will be expressed as loss in milligrams per square centimeter exposed, computed to the basis of one year as the time unit. The ideal method of expressing the results of corrosion would be a mathematical one involving the summation of the effects of all factors. Unfortunately the necessary equations have not been determined, nor can they be formulated at this time, due to the many possibilities of variations in the effects of the various factors under differing conditions.

THE CHEMICAL COMPOSITION OF THE METAL OR ALLOY.

This is by far the most important of all the factors. If the chemical composition of the metal or alloy is such that corrosion does not occur under any conditions, then the corrosion rate is zero. Such a composition is ideal, and is not now attained. For certain specific conditions it may be approximated, and the corrosion rate kept very low.

Since iron and steel are the most important of all metals,

and since iron rusts so readily, there have been many attempts made to change the composition so that iron alloys will not rust. It is beyond the scope of this paper to review these attempts.

The iron and steel alloys which have been found resistant to corrosion in a number of corrosive media include high silicon cast irons, chromium irons and chromium steels, chromium-silicon steels, chromium-nickel-silicon steels and perhaps others. Where alloys of the above types are made, the cost is necessarily increased over the lower-priced ordinary iron and steel. By increasing the degree of purity of the iron, the corrosion rate of very low carbon iron has been retarted for corrosion under certain conditions.

Since one of the marked differences in the composition of steels is in the carbon content, and since a change in the carbon content produces such a marked change in the physical properties of steel, all other constituents remaining constant, it was decided to test a series of steels for their resistance to various kinds of corrosive attack. The author realizes that many experiments of this kind have already been made, yet it seemed necessary to make tests because of lack of agreement in testing methods and in results, as reported by various investigators.

The following description of the methods of preparing the test pieces before testing, and cleaning them after testing is the general method employed in all the tests reported

in this paper.

PREPARATION OF SPECIMENS, METHODS OF CLEANING AND OF TESTING.

Steel cylinders about 2 inches long by 1/2 inch in diameter were cut from annealed rods of steel of varying carbon content. The carbon contents of all the steels used are given in the tables. Two alloy steels, cast chromium, and specimens of steel protected by chromium plate, and iron-chromium plate[(a)], were included in the list of materials to be tested.

(a) The technique of the plating of chromium plate and iron-chromium plate upon steel is discussed in a paper to be given before the American Electrochemical Society at the Fall meeting, 1925. See part II of this thesis.

The samples were prepared as follows:-

The surface "skin" was removed in one of three ways, (1) by careful machining, (2) by pickling, (3) or by using a scratch brush. In the atmospheric and distilled water tests, the pieces were machined. In later work the other methods were used. After any one of the preliminary treatments, the surface was rubbed with fine emery paper, and then wiped with cheese cloth. Whenever the pickling method was used, care was taken to neutralize and thoroughly wash and dry the specimens. One end of each specimen had a number or letter stamped lightly upon it, as a distinguishing mark. In the other end a hole about 1/4 inch deep was drilled and an aluminum wire was inserted. The diameter of the hole was such that the wire fitted in snugly, and a blow or two of a punch swaged the steel

about the wire. In the case of steels which could not be easily drilled, such as that steel designated as Cr-V, a copper wire was soldered to the end of each piece. The wires were cut to a length dependent upon the kind of test which they were to be given. The wire and end of the specimen were covered with paraffin, thus preventing the possibility of an electrolytic couple being formed by the dissimilar metals in the corroding medium. Sufficient wire was left exposed to bend into a hook, or to insert in the chuck of the rotating spindle of an electrolytic machine. The rate of corrosion of aluminum or of copper in air is known to be very small. Each specimen had approximately the same length of bare wire exposed to the air, in each test, and the corroding medium could act only on the test-piece on one end and the cylindrical area. Thus the error, if any, was nearly a constant. After preparation in this way, the surface of the metal was cleaned in an alcohol-ether mixture, dried at a low temperature and transferred to a dessicator. The test pieces were then measured, weighed and exposed. After the surfaces were cleaned the balance of the operation was carried on as rapidly as possible.

In all tests the method of cleaning was the same, as follows: At the end of the test the pieces were washed in tap water to remove loosely adhering corrosion product. They were than immersed for a few minutes in a dilute solution of ammonium acetate. This tended to loosen any rust which was

more firmly attached. No other chemical was employed, nor was any harder object than a piece of rubber or wood used to scrape the piece. Care was taken to avoid chipping or disturbing the paraffin. After washing in water the exposed metal, (but not the paraffin) was dipped for a few seconds in clean ether-alcohol mixture. The specimens were than dried in an electric oven at a temperature below the melting point of paraffin, for about ten to fifteen minutes. They were then transferred to a dessicator and allowed to cool to room temperature before weighing.

Exceptions to the methods described above will be noted later.

Test specimens in either triplicate or duplicate were exposed to the action of the atmosphere upon the roof of the building, and similar sets were exposed in distilled water within the building. A part of the set of specimens were tested in other ways, as will be discussed later.

Specimens were exposed to the air in the following manner: A wooden frame with wooden cross bars was prepared with the following dimensions, 18 by 30 by 12 inches. The cross bars were about 1/2 inch square and were placed 3-1/2 inches apart. The aluminum wire hooks were bent around these bars so that each specimen was separated from its neighbors by at least three inches. The rack was placed on the roof in such a position that it was fully exposed to light, and to the elements. Figure (1) is a view of a test piece as prepared

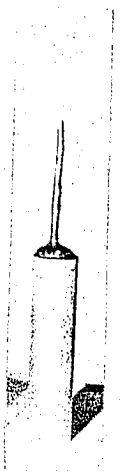


FIGURE (1): View of a test-piece prepared for exposure in atmosphere or in distilled water.

for exposure in either the atmospheric or distilled water test. Figure (2) is a view of the rack and specimens.

The test specimens in the distilled water tests were exposed as follows: Each specimen was suspended by its hook from a glass rod placed across the top of a 600 c.c. beaker; 500 c.c. of distilled water was added, and fresh water added from time to time to replace that lost by evaporation. The specimens were immersed to such a depth that about one inch of wire was immersed. No attempt was made to purify the distilled water, or to rid it of dissolved oxygen. Free access of light and air was allowed the beakers, but they were not exposed to direct sunlight.

Table I gives the rate of corrosion of the steels in the atmospheric corrosion of the steels in the atmospheric test, and Table II the rate of corrosion in the distilled water tests. The nature of the corrosion is given in the discussion.

DISCUSSION OF THE ATMOSPHERIC TESTS.

It was observed that all of the samples except the cast chromium, the chromium plate and the iron-chromium plate, showed tarnish after 24 hours exposure. At the end of 7 days all of the specimens, with the exception of the above-mentioned group, were completely covered with a layer of brown rust.

In cleaning, it was observed that all of the steels with the exception of those protected by chromium or iron-

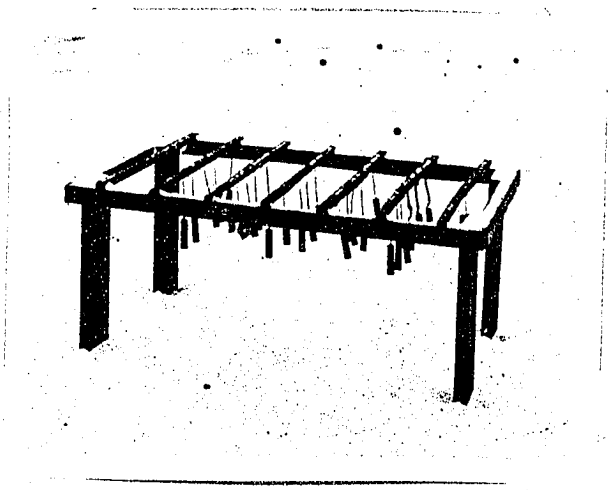


FIGURE (2): View of test-rack and specimens used in atmospheric tests.

TABLE I.

The corrosion of various steels in the atmosphere.

Sample No.	Steel No.	Time in hours.	WEIGHT IN GRAMS. before IMMERSION.	after	loss	Dimensions in inches. diam.	length	Area in sq. cm.	Loss in Mg. per sq.cm. per year.	Average loss	Deviation
01	0	1125	51.2017	50.9122	0.2895	.500	2.00	21.53	1065		
03	0	"	51.3068	51.0000	0.3068	.500	2.00	21.53	1108	1087	± 22
T151	.18	"	50.4267	50.1057	0.3210	.498	1.97	21.12	1184		
T152	.18	"	50.5269	50.1965	0.3304	.498	2.00	21.42	1200	1192	± 8
41	.5	"	51.1894	50.9587	0.2307	.500	1.94	20.90	858		± 13
42	.5	"	51.3831	51.1629	0.2202	.496	2.00	21.32	804		± 41
43	.5	"	50.4538	50.2260	0.2278	.500	1.88	20.28	874	845	± 29
61	.7	"	48.5045	48.2949	0.2049	.500	1.88	20.28	804		± 19
62	.7	"	48.5664	48.3803	0.1861	.504	1.75	19.14	753		± 34
63	.7	"	46.5783	46.3793	0.1990	.504	1.75	19.14	804	787	± 19
91	.9	"	50.6348	50.3647	0.2701	.503	1.94	21.00	1000		± 20
92	.9	"	46.7919	46.5458	0.2461	.503	1.78	19.45	984		± 36
93	.9	"	46.2605	45.9931	0.2674	.510	1.75	19.35	1075	1020	± 55
121	1.2	"	55.2589	55.7300	0.2289	.498	2.00	21.42	831		
123	1.2	"	54.9300	54.7142	0.2158	.498	1.93	20.80	807	819	± 12
X61	Cr plate	"	49.3098	49.3088	0.0010	.500	1.97	21.20	0.37		± .83
X62[a]	"	"	50.7905	50.7847	0.0058	.500	2.00	21.33	2.1		± 1.0
X63	"	"	50.8508	50.8485	0.0023	.500	2.00	21.53	.83	1.10	± .27
R61	Cr-Fe plate	957	52.5784	52.5495	0.0289	.500	2.00	21.53	12		
R62	"	"	50.7931	50.7916	0.0015	.500	2.00	21.53	.64	6.32	± 5.68
S21	Cast Cr	"	43.6067	43.5872	0.0195	too irregular to measure.					
S22	"	"	37.7292	37.7107	0.0185	too irregular to measure.					
S24	Cr-V	"	48.8829	48.7255	0.1574	.506	1.94	21.18	68		
S25	Ni-Si	"	95.9788	95.8505	0.0683	.880	1.25	23.49	27	39.5	± 12.5
S26	"	"	94.6580	94.5248	0.1332	.886	1.25	23.68	52		
T154	.18	24	50.1125	50.1101	0.0024	.500	2.00	21.53	41		
T155	.18	48	49.2728	49.2697	0.0031	.499	2.00	21.49	26		
T156	.18	72	49.5226	49.5220	0.0006	.495	2.03	21.60	3.3		
T157	.18	168	53.3712	53.3466	0.0246	.500	2.25	24.07	53		
T158	.18	168	49.7712	49.7433	0.0279	.498	2.06	22.01	66	60	± 6

([a]) Both ends paraffined.

TABLE II.

The corrosion of various steels in distilled water. Time - 504 hours. Room temp. 500 cc. of solution used.

Sample No.	Steel No.	WEIGHTS IN GRAMS. before IMMERSION.	after	loss	DIMENSIONS: IN INCHES. diam.	length	Area in sq. cm.	Loss in mg. per sq.cm. per year.	Average loss.	Deviation
04	0	50.8612	50.7348	0.1264	.500	2.00	21.54	102		± 5
05	0	50.8346	50.6837	0.1509	.500	2.00	21.54	122		±15
06	0	50.6695	50.9495	0.1200	.500	1.98	21.54	97	107	±10
T111	.18	50.2271	50.1180	0.1091	.497	2.00	21.39	89		± 3
T112	.18	49.9769	49.8655	0.1114	.497	2.00	21.39	91		± 1
T113	.18	50.2333	50.1143	0.1190	.497	2.00	21.39	97	92	± 5
44	.5	50.5061	50.4111	0.0950	.497	1.97	21.08	78		± 6
45	.5	51.3630	51.2561	0.1069	.505	1.95	21.25	87		± 3
46	.5	52.1149	52.0074	0.1075	.506	1.97	21.50	87	84	± 3
64	.7	47.6182	47.5224	0.0958	.502	1.86	20.18	83		± 2
65	.7	45.9658	45.8793	0.0865	.503	1.75	19.10	79		± 6
66	.7	49.4791	49.3676	0.1115	.500	1.94	20.90	93	85	± 8
94	.9	47.3966	47.3027	0.0939	.501	1.94	20.95	78		±22
95	.9	53.3098	53.1990	0.1108	.508	2.00	21.90	88		±12
96	.9	48.6083	48.4517	0.1566	.510	1.88	20.69	132	100	±32
124	1.2	54.7217	54.6250	0.0967	.500	1.95	21.01	80		± 6
125	1.2	54.8111	54.7136	0.0975	.498	1.95	20.91	81		± 5
126	1.2	57.2598	57.1411	0.1187	.501	2.00	21.58	96	86	±10
X1	Cr-plate	50.3962	50.3743	0.0219	.501	1.98	21.50	18		± 3
X20	Cr-plate	51.3805	51.3793	0.0012	.501	2.00	21.58	1		± 20
X13	Cr-plate	50.4533	50.4000	0.0533	.501	2.00	21.58	43	21	±22
R1[a]	Cr-Fe plate	49.3172	49.3000	0.0172	.500	2.00	21.54	14		± 1
R2[a]	Cr-Fe plate	50.8392	50.8274	0.0118	.500	1.94	20.90	10		± 5
R3[a]	Cr-Fe plate	50.7085	50.6839	0.0246	.500	2.00	21.54	20	15	± 5
S1	Cr-V steel	50.2548	50.1882	0.0666	.507	1.94	21.24	55		
S2	Cr-V steel	50.7929	50.7306	0.0623	.506	2.00	21.79	50	53	± 3
S3	Ni-Si steel	95.1959	95.6772	0.1187	.880	1.25	26.55	78		
S4	Ni-Si steel	96.3848	96.2835	0.1013	.885	1.25	27.05	65	72	± 7
S5[aa]	Cast Cr.	55.1161	55.1075	0.0086	irregular		-	-		
S6[aa]	Cast Cr.	128.8456	128.8333	0.0132	irregular		-	-		

([a]) Immersion 500 hours. ([aa]) Immersed 651 hours.
Remarks on the condition of test pieces at conclusion of test:- T111, Had some rust not removable . 94, 95 & 96, spotted with brown lacquer - like areas. X1, Rust at edge. Body O.K. X20, no noticeable rusting. X13, Considerable rusting. R1, R2 & R3, rusted through pin holes in plates. S3 & S4, Measurements were approximate only. All other specimens showed only a normal amount of colloidal rust, which was easily removable.

chromium plate, formed very adherent layers of rust, which were removed only with difficulty. Cast chromium, showed no evidence of tarnish or attack. So uniformly did the rusting take place on the steels that it is not necessary to comment in the table on any special pieces. Originally all the samples except cast chromium were exposed in duplicate or triplicate, but through failure of the support, or for some other reason, the record does not show losses in duplicate or triplicate for all specimens. In cleaning it was found necessary to brush the specimens after drying with a stiff bristle brush to remove some of the rust still remaining. After the final brushing, the condition of the pieces was comparable to that of the pieces in the distilled water tests after cleaning.

It should be emphasized that the duration of the atmospheric tests was comparatively short. In this, as in all other tests made in this investigation, the object was to observe the effects of the various factors and to determine the rate of corrosion in the INITIAL STAGES of the corrosion attack. Hence no attempt was made to corrode any specimens to failure.

In the atmospheric tests, as in the others, pitting did not seem to be generally prevalent. Pitting developed through pin holes in some of the plated specimens. Aside from that it would seem that pitting is a later developement in the process, in cases where it developes at all.

DISCUSSION OF THE DISTILLED WATER TEST.

The specimens were all attacked within a short time, except the cast chromium, chromium plated and iron-chromium plated pieces. The ordinary carbon steels and the alloy steels would show weighable losses within 1 hour, and within 2 hours would show many yellow specks. Within 4 hours the water in the beakers had a distinctly yellowish tinge. Within 24 hours all of the carbon steels and the alloy steels were completely covered with a yellow-brown colloidal coating easily detached.

Notes on the appearance of the pieces at the end of the test are given in Table I. Carbon content is indicated by "steel No."

No special comment is needed on the corrosion of the steels of lower carbon content. While there are variations in the average losses, it cannot be said that any marked differences occur. With the 0.7 percent carbon steels, and one of the 0.9 per cent carbon steels, small areas differed from the rest of the specimens in color. The rust seemed to be cemented on, but no noticeable difference in the level on the piece occurred - that is, the areas did not appear either as pits or raised areas. No explanation can be offered for this difference in appearances, unless it might be that had the attack been carried further, pitting might have resulted. The rate loss is not sufficiently different in the case of these specimens to be significant.

The chromium-plated, and cast chromium specimens

showed the best resistance, as would be expected. The alloy steel, Cr-V did not show as marked a superiority over the carbon steels as might have been expected from its high chromium content. The iron-chromium plated specimens showed a low rate loss, but were badly pitted - that is, many pin holes not originally visible in the plate had developed and allowed corrosion of the steel beneath to proceed. The Ni-Si steel shows a slightly lower loss rate than the ordinary carbon steels.

This test shows that in distilled water there is no marked difference in the corrosion rate which can be traced to the influence of the carbon content of the steel. As would be expected, where chromium is added, whether as a plate, or an alloy plate, or as a constituent of the steel, the corrosion rate is retarded. Figure (3) is a view of a Fe-Cr plated specimen, showing corrosion through pin holes.

Steels of the "Stainless Steel" type and many other Cr alloy steels have been so widely tested[56,42] and found resistant that extensive tests were not deemed necessary here.

COMPARISON OF THE ATMOSPHERIC AND DISTILLED WATER TESTS.

The order of relative corrosion losses is remarkably good if we take into account the deviations from the average.

In Table III is given a direct comparison between the two tests.

It is evident that in the case of the ordinary carbon steels, that the carbon does not change the relative order of

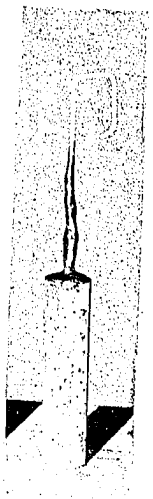


FIGURE (3): View showing pin holes and rust on a steel specimen plated with chromium-iron alloy.

TABLE III.

Comparison of average losses in the atmospheric and distilled water tests on a selected group of steels.

Steel No.	ATMOSPHERIC. Average loss in: per sq. cm. per year.	Average deviation.	Rank.	DISTILLED WATER. Average loss in mg. per sq. cm. per year.	Average deviation.	Rank.
.0	1087	±	22	8 or 9	107	±10	10
.18	1197	±	8	10	92	± 3	8 or 9
.5	845	±	28	6 or 7	84	±4	5,6 or 7
.7	787	±	24	5	85	±6	5,6 or 7
.9	1020	±	37	8 or 9	100	±22	8 or 9
1.2	819	±	12	6 or 7	86	±7	5,6 or 7
Cr-plate	1.08	±	.68	1	21	+18	1 or 2
Cr-Fe plate	6.32	±	5.68	2	15	±4	1 or 2
Cr-V	6.8	±	---	4	53	±3	3
Ni-Si	39.5	±	12.5	3	72	±7	4

corrodibility in either test. In the atmosphere the corrosion rate seems to be about ten times that in distilled water, but it is necessary to consider the time relationships, in this connection, and these will be discussed later. While the rank for the various steels is given, it is to be noted that for the ordinary carbon steels there is but little difference in the rates.

The effect of Cr, Si, and Ni, in retarding the corrosion rate is indicated by the comparisons in the table. Neither the Cr-V steel or the Ni-Si was chosen as a material definitely known to be corrosion resistant, though it was expected that the Cr-V steel would probably be fairly resistant. It was expected of course, that the Cr plates, and probably the Cr-Fe plates would be quite resistant.

SUMMARY ON THE EFFECT OF CHEMICAL COMPOSITION UPON THE CORROSION RATE OF METALS AND ALLOYS.

The tests just discussed show that there is no marked superiority of one kind of steel over another which can be traced to the carbon content.

In the distilled water and atmospheric tests, chromium bearing materials show considerable superiority to other materials. The effect of Ni-Si is also noticeable in retarding corrosion rate.

Review of the literature shows that the effect of chromium upon steel is very marked in increasing the corrosion resistance. In comparison with other materials this is very

marked. P. E. Armstrong[42] has summarized the work done by R. J. Anderson, J. R. Adams, and the author[47] while with the U. S. Bureau of Mines at Pittsburgh, as it applied to the effect of chromium in retarding corrosion in mine waters. This summary is quoted below:

1. A low-carbon chromium alloy possesses resistance to corrosion equal to pure lead; the weight loss for the two materials is less than that for any others.

2. With the same silicon, but higher chromium and carbon content, the loss is greater, due undoubtedly to the higher carbon.

3. A cast nickel-chromium-tungsten alloy and a low carbon iron alloy containing high nickel and chromium with some molybdenum showed losses far greater than the above chromium-silicon steels.

4. A very high chromium, low-carbon and low-silicon steel shows a loss higher than the steels under (1). This may be ascribed to the low silicon or perhaps to oxides, if the steel was made by addition of chromium through the reduction of its oxide in the steel-making furnace.

5. Tests of nickel-chromium-silicon steels show clearly the effect of increasing the nickel content when the chromium percentage is close to 10.

"Under these circumstances the author is convinced from his own study and from the general trend at this time that the rustless irons of the future, if the chromium alloy type is adhered to, will contain about 17 per cent of chromium and an added element with iron. The added element may be silicon, nickel, molybdenum, or various other elements, all of which serve a very useful purpose."

A survey of the literature, plus the experimental work of the writer, seems to indicate that the most promising field of research in the search for corrosion-resisting alloy steels or irons lies in the chromium type, with such additions as may be needed to confer desirable physical properties providing the additional added element does not lower the corrosion resistance.

Since the cost of chromium-alloy steels is relatively high, it would be desirable to have on the surface of a steel the corrosion-resisting properties possessed by a chromium-alloy steel. The experiments of the writer to obtain such a surface upon ordinary steel by means of a combination of plating, chromium heat-treating and cementation by carbon will be given in part II, , but it may be noted that the attempt has so far been unsuccessful.

PHYSICAL CONDITION OF THE METAL OR ALLOY.

It is well known that the physical condition of the metal or alloy has an important effect upon the corrosion rate, and the corrosion of a metal is intimately associated with the formation of local electrolytic couples at the surface in contact with an electrolyte. Also, other conditions being the same, sand-cast metals and alloys corrode more rapidly than the same materials when worked-and-annealed, and cold-rolled metals corrode more rapidly than annealed ones. The effect of the physical condition of a metal or alloy has been discussed at length by Desch[56]. R. J. Anderson and the author have investigated the effect of

grain size upon the corrosion of brass[44], and also the coatings formed upon corroded metals and alloys[45], when the surfaces differed by being in the "as-cast" or in the "machined" state. In the present work no further investigation was made of this factor. Care was taken to have all the specimens thoroughly annealed, and the surface of all specimens in as nearly the same condition as could be done.

The physical variables included under the general head of "physical condition" of the metal include grain size, hardness, condition of the surface (smooth, polished, or rough), amount of strain, strength, electrical conductivity, and the method of preparation of the sample as cast, worked, or annealed. Other variables might be mentioned. To investigate so many variables is beyond the scope of this thesis.

Chemically, a metal may be homogeneous or heterogeneous, but it is rarely physically homogeneous, and industrial metals and alloys are generally both chemically and physically heterogeneous. Chemical heterogeneity may come from impurities in a metal or alloy, from the presence of inter-metallic compounds or eutectics, or from coring in the case of solid solutions. Physical heterogeneity is owing principally to strains in the metal, for example, casting strains or working strains and cast metals may be porous. Heterogeneity would normally be a stimulant to corrosion because of the formation of electrolytic couples. In a chem-

ically heterogeneous metal or alloy, local electrolytic couples are set up on contact with an electrolyte because of the difference in potential between areas of different composition; while in a physically heterogeneous metal couples are set up between areas strained more and ones strained less. In the case of chemical heterogeneity, selective corrosion may result, one constituent being corroded in preference to others in the case of certain electrolytes, and depending of course on the composition and concentration of the electrolyte.

THE CHEMICAL COMPOSITION, CONCENTRATION, AND PHYSICAL CONSTITUTION OF THE CORRODING MEDIA.

The chemical composition of the corroding medium is an important factor in corrosion, and the variables which are inherent in the medium are its chemical composition (concentration) and its physical constitution. The latter includes viscosity and the amount of suspended matter, if any. The loss of electrons from the atoms of a metal to the atoms of a corroding medium (or better, the electron sharing between the atoms) depends upon the nature of their separate atoms and their electron configurations. Probably also, the arrangement of the atoms in the space lattice of the metal may affect the nature of the electron inter-change. The reason why platinum corrodes slightly in damp atmospheric acid while iron corrodes completely to an hydrated oxide can be found only in the potential energy of the atoms of these metals - that is, in the electron configuration and the arrangement in the space lattice - and the tendency towards electron

interchange with O^{--} and OH^{--}. It is beyond the scope of this paper to discuss the various types of interactions between metals or alloys and corroding media, but it is desired to emphasize that reactions are dependent primarily upon the metals and the media.

In the present investigation tests were made on steels in atmospheric air, in distilled water under various conditions, in dilute sulphuric acid, and in ferric sulphate and sodium chloride solutions. Analyses of these solutions are given in Table IV. In the atmospheric tests the corroding media was atmospheric air, with such variations in composition, concentration, etc., as might be expected in the winter season. In the distilled water tests, free access of air was allowed to the water. There is no question but what the oxygen of the air, dissolving in the corroding media, exerts a powerful influence, usually acting as a depolarizer in removing hydrogen from the metal surface. In this connection it may be noted that Speller[33] has found that the oxygen content of natural waters is an index of corrosion rate in such waters.

It is in the consideration of this factor that the effect of colloids upon the acceleration or inhibition of the corrosion rate is noticed. Colloidal solutions of metals may have considerable activity as catalysts. In electrolytes there is preferential adsorbtion of certain ions by the particles, and the sign of the colloid is dependent upon the degree

TABLE IV.

Analyses of solutions used as corrosive media in accelerated testing.

Solution.	Composition Desired	Actual.
H_2SO_4	4000 ppm.	3880
$Fe_2(SO_4)_3$	40000 ppm.	41100
NaCl	3.5 %	3.68 %

ppm. = parts per million, or milligrams per liter.

The composition for NaCl is per cent by weight.

of adsorption. Thus in cases of corrosion in electrolytes, a colloid will act as an accelerator or retarder of the corrosion rate depending upon the nature of the colloid and the number of ions present.

In Table V are given data upon the corrosion of 0.18 per cent carbon steel in distilled water and in dilute H_2SO_4 at different velocities and with varying amounts of gelatine.

When a considerable amount of a colloid such as gelatine is present, the solution may be rendered very viscous. In cases where the viscosity is great enough, and the nature of the material such that abrasion could occur, it would be difficult to distinguish between abrasion and true corrosion. In considering the data recorded in Table V, the effect of abrasion can be neglected and only the effect of the colloid considered.

The tests were carried out as follows: Specimens prepared in the same manner as previously described, but with shorter stems, were rotated in beakers, one specimen to each beaker. Each specimen was completely immersed. The other conditions are given in the table.

It will be noted that the effect of the gelatine is to greatly retard the corrosion rate, and that increasing the gelatine content within the limits given in the table decreases the corrosion rate in the dilute sulphuric acid solution, and in distilled water.

The viscosities were measured by means of a 50 c.c. pipette with a capillary tip, no viscosimeter being available.

TABLE V

The effect of velocity and viscosity upon the corrosion rate of 0.18 % carbon steel. Time immersed, 4 hours. Room temperature. 250cc of solution used per sample.

Sample No.	Speed of rotation R.P.M.	Weights in grams before immersion	Weights in grams after immersion	loss	Dimensions in inches diam.	Dimensions in inches length	Area in sq. cm.	Loss in mg.sq.cm. per year.	Average loss.	Deviation.
T2	100	50.5748	50.4462	0.1286	.499	2.00	21.49	13100		
T3	100	49.0538	48.9716	0.0822	.498	1.94	20.81	8620	10860	±2240
V1	140	50.2584	50.1557	0.1027	.500	2.00	21.54	10446		
V2	140	49.3562	49.3217	0.0345	.499	2.00	21.49	3520	6980	±3460
V3	200	48.1525	48.1043	0.0482	.495	1.94	20.68	5100		±2110
V4	200	49.9571	49.8683	0.0888	.499	1.94	20.87	9320	7210	
V5	140	50.7961	50.7950	0.0011	.500	2.06	22.04	110		
V6	140	51.3605	51.3545	0.0060	.499	1.94	20.87	630	370	±260
V7	140	49.9725	49.9571	0.0154	.498	1.94	20.81	1620		
V8	140	53.4312	53.4087	0.0227	.500	2.25	24.07	2060	1840	±220
V9	200	50.1557	50.1336	0.0221	.500	2.00	21.54	2250		
V10	200	49.3217	49.3010	0.0207	.499	2.00	21.49	2110	2180	± 70
V11	140	50.7138	50.6935	0.0203	.499	2.00	21.49	2070		
V12	140	50.6581	50.6402	0.0179	.500	2.00	21.54	1820	1945	±125
V13	200	53.4085	53.3920	0.0165	.500	2.25	24.07	1500		
V14	200	51.3545	51.3347	0.0198	.500	2.06	22.04	1970	1735	±235
V15	140	48.1565	48.1525	0.0040	.495	1.94	20.68	420		
V16	140	49.4489	49.4461	0.0028	.498	1.94	20.81	295	357	± 62
T6	100	49.9494	49.9361	0.0133	.499	1.97	21.17	1380		
T9	100	50.3191	50.3075	0.0116	.499	1.97	21.17	1200	1290	± 90

NOTE:- Solutions used were as follows

T2, T3, V1, V2, V3, &V4-- dilute H_2SO_4 (3880 parts per million)

V5&V6, 5 gr. gelatine to 250 cc distilled H_2O"

V7, V8, V9, &V10-- 0.5 gr gelatine/to 250 cc dilute H_2SO_4

V11, V12, V13 & V14- 2.5 gr. gelatine to 250 cc dilute H_2SO_4

V15 &V16-- 12.5 gr gelatine to 250 cc dilute H_2SO_4

T6 & T9-- distilled H_2O

The dilute H_2SO_4 used in these runs contained 3880 parts per million free H_2SO_4

The same pipette was used, and the temperature of the solutions was the same, and also the pressure, so that the viscosities are comparable on a time basis. The viscosities are given in Table VI..

FILMS AND COATINGS.

Films and coatings formed on metals and alloys result from the interaction of the metal and the corroding medium, or by precipitation from the medium. R. J. Anderson (45) and the author have discussed this factor elsewhere, and have noted that distinction should be made between films and coatings, and have suggested that a film be defined as a corrosion product or deposition on the surface of the metal of such thickness that it can not be measured by the metallurgical microscope, and that a coating be regarded as a product or deposition that can be measured microscopically or by less exact methods.

Evans (43) has studied the relation between tarnishing and corrosion. He distinguished between tarnishing and the products of corrosion formed in water or electrolytes, in that the tarnish is a film in optical contact with the metal, whereas the ordinary corrosion in the presence of moisture gives less adherent films, or in other words, that tarnish, formed, for example, on dry copper exposed to dry hydrogen sulfide is a film IN SITU but the addition of a film of liquid water causes the formation of a non-adherent layer of black or brown sulfide.

TABLE VI.

Viscosities of gelatine solutions.

Amount of gelatine	Average time in seconds required to empty 50 c.c. pipette.
None ($dil.H_2SO_4$).	125
.5 gr. gelatine to 250 c.c. ($dil.H_2SO_4$).	128
2.5 gr. gelatine to 250 c.c. ($dil.\ H_2SO_4$).	175
12.5 gr. gelatine[a] to 250 c.c. ($dil.\ H_2SO_4$).	300

([a]) Solution became extremely stiff during the period of the test.

While the composition of the metal and that of the corroding medium are the most important factors in the formation of films and coatings, other factors including the nature of the metal surfaces (whether rough or polished) and the velocity and temperature of the corroding medium are also important. Films or coatings may retard or accelerate corrosion rates, depending in part upon the degree of imperviousness of the film or coating and upon the intimacy of contact with the metal.

In the work here reported all the coatings were so loosely adherent that no retarding effect would be expected, indeed, the coatings formed may have had an accelerating effect. Films may have been formed upon the surface of cast chromium, and on the chromium and iron-chromium plates, but no attempt was made to determine this point.

VELOCITY OF THE CORRODING MEDIUM.

The velocity of the corroding medium about a metal (or what amounts to the same thing, the velocity of the metal in the medium) is a variable factor which affects corrosion rates. First, the speed at which a corroding medium passes over the metal and the amount of suspended matter therein may cause erosion losses which cannot be distinguished from corrosion losses. Second, if the solution is constantly changing owing to movement and new medium is coming in contact with the metal as old solution passes away, then there is continued renewal of solution so that the concentration remains the same. If the solution is at rest and of small bulk as in laboratory

immersion tests, then the concentration of the solution decreases. Thus, as a solution decreases in concentration the rate of corrosion may increase or decrease depending upon the medium.

It has been shown by Heyn and Bauer[62] that if iron is allowed to corrode slowly in moving water, the rate of corrosion first rises rapidly with increase in the rate of flow, but after reaching a maximum further increase in the velocity of the water causes a fall in the corrosion rate. It has also been found by Friend[27, 3] that in water with a velocity up to six miles per hour, the corrosion at first increases with increasing velocity, then falls to a minimum at about two miles, and then finally slowly increases. In sulphuric acid, however, the corrosion rate increases with increasing velocity (i.e., is directly proportional) and different concentrations yield almost identical results at the same velocities. Dieterlen[63], in experiments on the rate of flow of water over circular steel discs, finds that the corrosion increases with increasing velocity up to a limiting velocity when the attack ceases. Friend[27] explains the difference in behavior of iron toward neutral and acid media when in motion by the auto-colloidal catalytic theory. Speller and Kendall[33] have examined the effects of velocity and temperature upon corrosion rates in the case of corrosion caused by tap water passed through steel pipe. In general, it was found that the corrosion rate increases with increasing velocity of passage but for some velocities at certain temperatures there was a decrease. This is

contrary to the results obtained by Heyn and Bauer and by Friend.

The effect of films and coatings in relation to the velocity on corrosion rates has been more or less overlooked, and a simple statement of the facts in the case is as follows: If an adhering coating is retarding corrosion at a certain velocity of the medium, then increase of the velocity, if it removes the coating, will accelerate the corrosion. And, on the other hand, if a coating is accelerating corrosion at a given velocity, then increase of the velocity will retard the rate. Loose coatings, or those which are readily dislodged, may be easily swept away by increasing the velocity of the medium over the exposed surface of the metal. In testing work, the velocity of the corroding medium can be made constant or variable so that its effects can be determined.

Tests were made upon 0.18 per cent carbon steel for the effect of velocity upon the corrosion rate in dilute H_2SO_4. The data is given in Table V. Only three speeds could be employed, owing to the limitations of the testing machines used. The method of testing was as follows: Duplicate specimens prepared in the usual way were completely immersed in dilute H_2SO_4 and rotated at constant speed during the 4 hour time period. Similar specimens were then rotated as different speeds. All specimens were cleaned and weighed as previously described. The data in the table is insufficient to draw definite conclusions, the deviations from the average values being great.

TEMPERATURE OF THE CORRODING MEDIUM.

Most chemical reactions are accelerated by increase of temperature, and in a general way corrosion rates increase with rising temperature. There are, however, many exceptions to this, and when there is an increase in the rate this is not necessarily a linear function of the temperature. Friend[3] finds that for polished iron foil immersed in distilled water the rate of corrosion increases to a maximum at about 80° to 84° C., but rapidly falls at higher temperatures, while Speller and Kendall[33] have found that in the case of pipe, through which city water is passed at different velocities the corrosion rate increases in general with increased temperatures.

In service, the temperature variation is usually not very great, but in special cases it may vary over a wide range and then becomes important. However, the temperature should be properly regarded as an important factor affecting corrosion rates, and in testing this may be readily varied to suit conditions.

Experiments were made on a series of 0.2 per cent carbon samples. These samples were polished and numbered in the usual manner but were not fitted with aluminum wires or parafinned. Tests were made in distilled water and in two solutions, dilute H_2SO_4, and $Fe_2(SO_4)_3$: The analyses of which are given in Table IV. Each specimen was immersed in 100 c.c. of solution and held at the desired temperature for one hour. The beakers and solutions and specimens were maintained at any

desired temperature below the boiling point, by placing them during the period of the test in an electric oven which could be regulated approximately to temperature. The specimens were easily cleaned of the loosely adhering coating and washed, dried and weighed in the usual way. The data is recorded in Table VII and the curves are plotted in Figure (4). From study of the data and the curves, it is seen that the increase in corrosion rate is a function of temperature between room temperature and boiling point. At the boiling point of the solutions, the losses were much greater, but the data is not plotted in Figure (4), since the factors are changing at the boiling point - that is, the change of phase changes the concentration and composition of the medium and also tends to liberate any dissolved gases. It is significant that the slope of the curves is so nearly the same for the temperature range investigated in three solutions which differ so widely in their chemical characteristics as ferric sulphate, dilute sulphuric acid and distilled water.

Tests were also made in dilute H_2SO_4, heating the specimen to different temperatures, allowing it to become saturated with heat at that temperature, and then plunging into 100 c.c. of dilute H_2SO_4 having a temperature of 20° C. The piece was then allowed to remain in the solution for one hour, and the temperature of the solution noted at the end of that time. The curves for the three solutions are nearly parallel, showing that within the temperature limits indicated, the effect of

TABLE VII.

The effect of variations in temperature upon the corrosion rate of .27% C. steel in dil. H_2SO_4, $Fe_2(SO_4)_3$ and distilled water. Constant factors. Time - 1 hour. Composition of solutions, see Table V. 100 cc. of sol. used per sample. Heated in electric oven.

Sample No.	Temp. Degrees C.	WEIGHTS IN GRAMS. before IMMERSION	after IMMERSION	loss	Dimensions in inches. diam.	length	Area in sq.cm.	Loss in mg. per sq. cm. per year	1/T°abs.	Log average loss.
1	2	3	4	5	6	7	8	9	10	11
				Dilute H_2SO_4.						
217	20	49.4298	49.4278	0.0020	.498	1.97	22.37	784	.00341	2.8943
213	32	49.1982	49.1947	0.0035	.497	1.97	22.31	1375	.00328	3.1383
227	85	49.0896	49.0225	0.0671	.499	1.97	22.41	26200	.00279	4.4183
211	55	48.6783	48.6683	0.0100	.498	2.00	22.70	3860	.00305	3.5866
219	67	49.1053	49.0898	0.0155	.499	1.97	22.41	6050	.00294	3.7818
216	80	49.2146	49.1854	0.0292	.497	1.97	22.31	11450	.00283	4.0588
27[a]	250 to 45	48.9510	48.9380	0.0130	.499	1.97	22.41	5080		
218[a]	175 to 38	49.3650	49.3600	0.0050	.497	1.97	22.31	1960		
215[a]	97 to 20	48.0970	48.0900	0.0070	.498	1.94	22.05	2780		
214[a]	80 to 20	47.2468	47.2435	0.0033	.497	1.91	21.82	1320		
28[a]	75 to 20	49.3049	49.3027	0.0022	.497	1.97	22.31	865		
29[a]	65 to 20	49.9104	49.9076	0.0028	.497	1.97	22.31	1100		

([a]) First temperature indicates temperature of specimen when plunged into 100 cc. dil. H_2SO_4 at room temperature. Second figure indicates temperature at end of solution at end of hour.

TABLE VII. (continued).

1	2	3	4	5	6	7	8	9	10	11
					$Fe_2(SO_4)_3$ Solution.					
220	17	48.9350	48.8713	0.0637	.499	1.97	22.41	24860	.00345	4.3955
221	39	49.3006	49.2207	0.0799	.497	1.97	22.31	31350	.00321	4.4962
223	65	49.9056	49.7548	0.1508	.498	2.00	22.70	58200	.00296	4.7649
224	73	49.4258	49.2690	0.1568	.498	1.97	22.37	61500	.00289	4.7889
225	85	49.3565	49.1483	0.2082	.497	1.97	22.31	81650	.00279	4.9120
226	45	48.0833	47.9682	0.1151	.498	1.94	22.05	45800	.00314	4.6609
					Distilled water.					
231	17	49.1923	49.1919	0.0004	.497	1.97	22.31	157	.00345	2.1959
232	39	47.2418	47.2418	0.0000	.497	1.91	21.82	000	.00321	
234	65	49.1788	49.1772	0.0016	.497	1.97	22.31	628	.00296	2.7980
235	73	49.0979	49.0956	0.0023	.499	1.97	22.41	899	.00289	2.9538
236	85	50.5017	50.4998	0.0019	.497	1.97	22.31	745	.00279	2.8722
237	45	49.1882	49.1874	0.0008	.497	1.97	22.31	314	.00314	2.4969

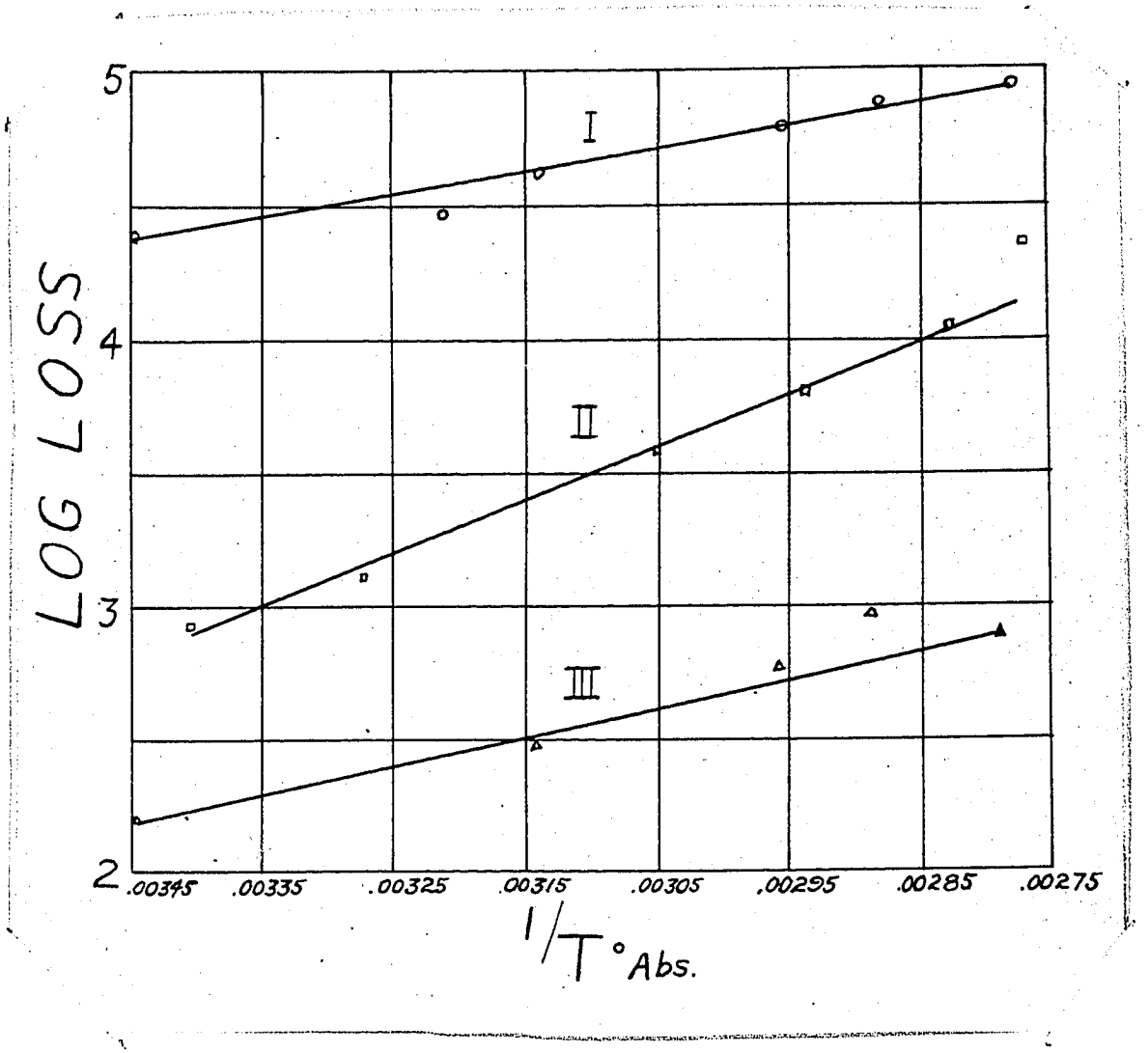


FIGURE (4): The relation between corrosion loss and temperature as affecting the corrosion rate of mild steel in $Fe_2(SO_4)_3$ solution (Curve I), dilute H_2SO_4 (Curve II), and distilled water (Curve III).

increasing temperature is in general, much the same, irrespective of the solution.

TIME PERIOD OF EXPOSURE.

In general, it is usually considered that the greater the time period of exposure of a metal to a corroding medium the greater the amount od corrosion; or, if a metal is exposed for a long time, the loss will be greater than if exposed for a short time. In the main this is true, but it does not necessarily imply that the corrosion rate is constant and that the rate of loss during the first 5 minutes of exposure may be the same as for a 5 minute period after the sample has been exposed several hours. The fact that corrosion rates vary during exposure is owing to the effect of films and coatings formed which may accelerate or retard corrosive action. Hence, a corrosion rate over a short period of time may be a linear function of the time but it would not be expected to be over a long period of time. Thus, the expression for corrosion loss over a period of time gives simply the average loss over that time and not the actual rate during any given period of time. A metal may have a rapid corrosion rate when first exposed to a medium, and then the rate may decrease or increase owing to the retarding or accelerating effect of films or coatings formed.

The foregoing points are well illustrated by the following experiments:

EXPERIMENT I. - Specimens of 0.18 per cent steel (cylinders 1/2 inch diameter by 2 inches in length approximately) were prepared as previously described but were not fitted with aluminum wires and paraffin except in the case of samples T111, T112, and T113. The samples were immersed in distilled water in duplicate for the time periods of exposure indicated. After removal from the water they were cleaned, dried and weighed as previously described. The data is given in Table VII, and the figures are plotted in Figure (5). In every case the rust formed was easily removed, and no other features of interest were observed.

It is evident that the rate of corrosion under the conditions given - that is, steel corroding in still distilled water changes from time. During the initial stages the rate is very rapid, it then decreases, and reaches a minimum seven or eight days after exposure. After this the rate slowly increases.

EXPERIMENT II. - Specimens of 0.18 per cent carbon steel, similar in every respect to those described in Experiment I, except that they were all prepared with wires and one end of each paraffined, were exposed to the atmosphere under the same conditions as were the specimens described under atmospheric tests. The data is given in Table I, and is plotted in Figure (5).

As early as 24 hours after exposure "a tarnish" was evidenced, and a weighable loss in weight resulted from the

TABLE VIII.

The relation between time and corrosion loss on .18% carbon steel. Conditions: Cylindrical specimen just immersed in distilled water, both ends exposed. Room temperature, day and night. One end of specimen paraffined.

Sample No.	Time in hours.	WEIGHTS IN GRAMS. before IMMERSION	after	loss	Dimensions in inches diam.	length	Area in sq.cm.	Loss in mg. per sq. cm. per year.	Average loss.	Deviation.
T101[a]	8	50.4409	50.4346	0.0063	.499	2.00	22.75	303		
T102[a]	8	49.9293	49.9256	0.0037	.499	1.97	22.46	180	242	± 62
T103	24	52.1522	52.1472	0.0050	.499	2.00	22.75	80		
T104	24	50.8635	50.8577	0.0058	.499	2.00	22.75	93	87	± 1
T105	72	49.9395	49.9282	0.0011	.499	2.00	22.75	60		
T106	72	50.4973	50.4684	0.0109	.499	2.09	23.66	56	58	± 2
T107	96	50.8659	50.8482	0.0177	.499	2.09	23.66	68		
T108	96	50.2499	50.2391	0.0108	.499	2.00	22.75	43	56	± 13
T109	120	49.3259	49.3070	0.0189	.500	1.98	22.47	61		
T110	120	50.7330	50.7127	0.0203	.499	2.03	23.16	64	63	± 2
T111[b]	504	50.2271	50.1180	0.1091	.497	2.00	21.39	89		± 3
T112[b]	504	49.9769	49.8655	0.1114	.497	2.00	21.39	91		± 1
T113[b]	504	50.2333	50.1143	0.1190	.497	2.00	21.39	96	92	± 4

([a]) Test was in daylight only.

([b]) Data taken from Table II.

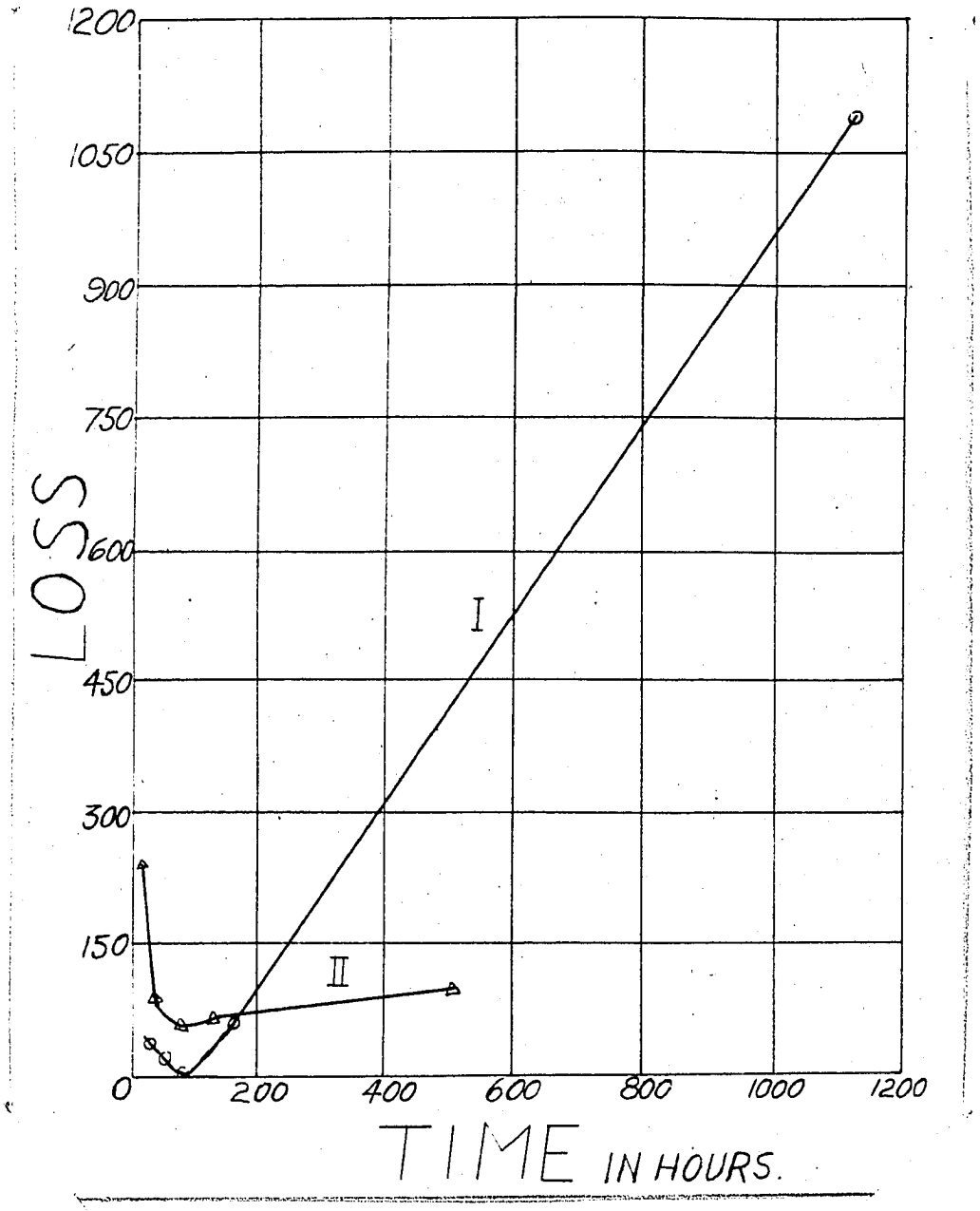


FIGURE (5): The relation between time and average corrosion loss (expressed in mg. per sq. cm. per year) for a mild steel corroded in the atmosphere (Curve I) and in distilled water (Curve II).

exposure. After 72 hours the specimens were well covered with rust.

In general, it may be said that the results of this test confirm those reported for Experiment I, and a minimum rate of corrosion is found at some point. The curves are very similar for the still-distilled water test, and the atmospheric test.

SOLUTION PRESSURE OF THE METAL.

Every metal has a certain solution tension or pressure tending to drive it into solution (in the ionic form) in an electrolyte, and the relation of the pressures of the metals is given by their order in the electromotive series. This series is shown in Table IX together with the potential differences in volts for normal solutions of cations. The series shows that the solution pressure becomes rapidly less on passing down from potassium to gold, and it also states that any metal will replace any one below it in the series from the ionic conditions in solutions of their salts. Thus, lead will replace copper and silver but not zinc and iron. The metals high up in the series corrode more readily when exposed to natural agencies air, water, and carbon dioxide than do those low in the series, but the order given is not indicative of the corrosion under all conditions. The electrolytic solution pressure concept as indicated by the electromotive series of the metals has been applied by adherents of the electrolytic theory of corrosion to explain the inception and process

TABLE IX...

Electromotive series and potential differences in volts.

Metal.	Volts.	Metal.	Volts.
K	(+ 2.9)	Ni	- 0.04
Na	(+ 2.54)	Sn (Sn^{++})	- 0.08 (?)
Ba	(+ 2.54)	Pb	- 0.13
Si	(+ 2.49)	H	- 0.28
Ca	(+ 2.28)	Cu (Cu^{++})	- 0.61
Mg	+ 1.21	As	- 0.62 (?)
Al	+ 1.00	Bi	- 0.67 (?)
Mn	+ 0.80	Sb	- 0.74 (?)
Zn	+ 0.49	Hg (Hg)	- 1.03
Cd	+ 0.14	Ag	- 1.05
Fe (Fe^{+++})	+ 0.06	Pd	- 1.07 (?)
Tl	+ 0.04	Pt	- 1.14 (?)
Co	- 0.04	Au	- 1.35 (?)

of corrosion, and the series lists the metals in the order of their tendency to pass into the ionic condition when placed in an electrolyte.

That metals can pass into solution in non-electrolytes has been demonstrated by Gates [24] and by others, and it has also been shown that it is possible to throw out metallic copper from non-aqueous, non-conducting solutions by means of many metals including lead, zinc, cadmium, tin, silver, iron, nickel, cobalt, and others. Hence, the replacing power of the metals is not a fixed property of the metals themselves but it is largely dependent upon the chemical nature of the solution in which the replacement occurs. Bengough and Stuart [15] cite the results of Gates, showing that metals are soluble in anhydrous non-conducting solutions, oelic acid for example, as proof that corrosion may be chemical in nature as contrasted with corrosion that takes place in electrolytes and which they characterize as electrochemical. The work of Gates simply shows that chemical reaction depends upon the atoms of the interacting substances on the basis of the electronic theory.

It should be pointed out that it is not safe to draw conclusions as to the corrodibility of alloys, on the basis of the place of the constituent metals in the E.M.F. series, since the potential difference (and hence the position of the alloy in the series) has not been determined for many alloys.

ELECTRICAL CONDITIONS OF IMMERSION.

The electrical conditions of immersion must be considered in the case of corrosion in electrolytes. Such conditions can, of course, be controlled in tests and in practice, but in testing it is not usually necessary to set up variable electrical conditions for the immersed metal. In service corrosion, for example, buried pipes or in soils, railway track, etc. stray electric currents may accelerate corrosion by the passage of a current through the metal and the surrounding electrolyte. In the case of parts in service, it has been found advantageous to impose a counter electro-motive force to the direction of current flow owing to the passage of the metal into solution, and a notable example of so counteracting corrosion is had in the Cumberland process.(40) The problem of stray currents as affecting corrosion rates and that of counteracting corrosion by setting up opposing electrical currents need not be given attention here, and it is sufficient to indicate that the effect of particular electrical conditions must be taken into consideration.

EFFECT OF LIGHT.

Light is a factor affecting corrosion rates, but the mechanism of its effects is not known. That exposure to diffused daylight accelerates corrosion has been shown by Cribb and Arnaud and by Friend(3); and the latter has found that the corrosion of iron foil in water when in the dark is about 85 per cent of that in the light. For practical pur-

poses, however, the effect of light may be neglected, and it can be controlled in testing. Still in the case of corrosion in mines it would be expected that the corrosion loss under definite conditions in the dark of a mine would be less than that in daylight.

To investigate this question a little more fully it was decided to corrode 0.18 per cent carbon steel specimens, and Cr-V steel specimens in distilled water under different conditions of light, but maintaining all other factors as constant as possible. Accordingly specimens were prepared in the manner previously described, and were placed in still distilled water under the following light conditions: Complete darkness, alternate day-light and darkness, complete daylight, red-light, ultra-violet light, and alternate ultra-violet light and darkness. Specimens were also exposed to the action of ultra-violet rays and air.

The temperature probably varied a few degrees in the longer tests, that is, the temperature of the solution varied. In the case of the specimens exposed to ultra-violet light, the temperature of the water increased slightly above room temperature, but it has already been shown that for the lower temperatures the effect of increase in the temperature of solution upon the corrosion rate is rather small. The period of exposure and other data is given in Table X. In the case of specimens L21, L22, L23 and L24, the alternation of ultra-violet light and darkness was as follows: 2 hours ultra-violet light, 16 hours in darkness, 8 hours ultra-violet light, 17 hours in

TABLE X.

The effect of different kinds of light upon the corrosion rates of steels in distilled water and air. One end of specimens paraffined.

Sample No.	Steel No.	Time in hrs.	WEIGHT IN GRAMS. before IMMERSION.	after	loss	Dimensions in inches: diam.	length.	Area in sq. cm.	Loss in mg. per sq. cm. per year.	Average loss	Deviation.
L1	.18	505	50.4724	50.3486	0.1238	.504	1.97	21.40	100		± 3
L2	.18	505	50.3000	50.1990	0.1010	.500	2.00	21.54	82		±15
L3	.18	505	50.8020	50.6633	0.1387	.503	2.00	21.87	110	97	±13
L4	Cr-V	505	48.1443	48.0700	0.0743	.507	1.88	21.54	60		
L5	Cr-V	505	50.6448	50.5620	0.0828	.505	2.00	21.76	66	63	± 3
T111	.18	504	50.2271	50.1180	0.1091	.497	2.00	21.39	89		± 3
T112	.18	504	49.9769	49.8655	0.1114	.497	2.00	21.39	91		± 1
T113	.18	504	50.2333	50.1143	0.1190	.497	2.00	21.39	96	92	± 4
L9	Cr-V	504	50.2548	50.1882	0.0666	.507	1.94	21.24	54		
L10	Cr-V	504	50.7929	50.7306	0.0623	.506	2.00	21.79	50	52	± 2
T101	.18	8	50.4409	50.4346	0.0063	.499	2.00	21.49	322		
T102	.18	8	49.9293	49.9256	0.0037	.499	1.97	21.20	192	257	±65
L13	.18	8	53.5980	53.5905	0.0075	.500	2.25	24.07	342		
L14	.18	8	51.4665	51.4634	0.0031	.500	2.06	22.04	154	248	±94
L15	.18	8	49.4711	49.4651	0.0060	.499	2.00	21.49	306		
L16	.18	8	50.2929	50.2850	0.0079	.499	1.97	21.17	408	357	±51
L17	.18	8	50.4611	50.4596	0.0015	.500	2.00	21.54	76		
L18	.18	8	50.9646	50.9631	0.0015	.500	2.00	21.54	76	76	± 0
L19	.18	8	48.9620	48.9580	0.0040	.498	1.94	20.81	210		
L20	.18	8	50.0920	50.0659	0.0261	.499	1.94	20.87	1370	790	±580
L21	.18	49	50.2220	50.2038	0.0182	.500	2.00	21.54	150		
L22	.18	49	49.8570	49.8411	0.0159	.499	1.97	21.17	134	142	± 8
L23	Cr-V	49	55.5192	55.5130	0.0062	.500	2.00	21.54	52		
L24	Cr-V	49	56.4805	56.4700	0.0105	.507	2.03	22.17	85	69	±17

Data on solution and light conditions: given on page 41b.

TABLE X(continued).

Samples L1, L2, L3, L4 and L5 were immersed in distilled water and kept in complete darkness.
Samples T111, T112, T113, L9 and L10 were immersed in distilled water and were alternately exposed to day-light and darkness.
Samples T101, and T102 were immersed in distilled water, and were exposed only to day-light.
Samples L13 and L14 were immersed in distilled water, and kept in absolute darkness.
Samples L15 and L16 were immersed in distilled water, and exposed to the action of red-light.
Samples L17 and L18 were exposed in air only to the action of ultra-violet-light.
Samples L19 and L20 were immersed in distilled water, and exposed to the action of ultra-violet light.
Samples L21 and L22, L23 and L24 were alternately exposed to the action of ultra-violet light, and kept in complete darkness. These samples were immersed in distilled water.

darkness, 6 hours in ultra-violet light. The tests in complete darkness were carried out in a photographic dark room, and the ultra-violet light experiments were carried on in another dark room. Red light was supplied in a printing cabinet, the red filter being placed in the position ordinarily occupied by the ground glass. Four bulbs of 40 watts each furhished the light.

Under all conditions of light, the Cr-V steel shows a lower rate loss than the 0.18 per cent carbon steel.

Although there is quite a large deviation, the ultra-violet light shows a marked accelerating affect upon the corrosion rate.

The difference between the losses in complete darkness and in daylight, or alternate day light and darkness, does not seem to be sufficient to warrant drawing a conclusion that darkness either accelerates or retards the corrosion rate under the given conditions. Red light seems to slightly accelerate the corrosion rate in the case of the 0.18 per cent carbon steel.

There is no doubt but what under certain conditions that the kind of light, or absence of light will affect the corrosion rate. Ordinarily the effect will be so small that it may be neglected in considering corrosion losses.

COMPARISON OF TESTING METHODS.

There is wide divergence of opinion as to proper method or methods of making corrosion tests. If the corrodibility of a metal is to be determined, it may mean the corrodibility (the nature and rate of solution) in some specific medium, or

it may mean the general resistance which the metal may have to corrosion.

Obviously the best test of the resistance of a metal to corrosion is the actual use of the material under service conditions in a specific corrosive medium. If quicker results are desired, or it is not practical to make such a test, some other means may be devised to test the metal.

It must be emphasized that there are so many variables affecting any corrosion process, that it is not safe to predict the results which may be expected in service, from the results obtained in laboratory tests, unless all the variable factors have been controlled. For example, stainless steel is known to be soluble in sulphuric acid (43). It might therefore be expected that stainless steels would be of small value in parts of mining machinery which are exposed to the action of acid mine water which contains considerable amounts of free sulphuric acid. Yet the opposite is usually true. Certain kinds of steels, high in chromium, (and in some cases other elements) are found to resist the action of mine water very well (46, 47). The explanation probably lies in the fact that ferric sulphate, an oxidizing agent, is much more active in corroding than the sulphuric acid. It may even tend to render the stainless steels passive.

On the other hand, monel metal known to be fairly resistant to the attack of sulphuric acid, has a relatively high rate loss, in mine water containing ferric sulphate (63).

Comparison of the results given in Table XI will show the high losses of ordinary steels in ferric sulphate solution as compared to a much lower loss in dilute sulphuric acid under similar conditions.

Many accelerated tests have been suggested and much work has been done on this phase of the problem. In the present investigation, the author used several methods of testing, and several corrosive media. As has been stated, the purpose of the investigation was to study the effect of various factors upon the nature of corrosion and the corrosion rate in the earlier stages of the corrosion progress. The corrosion media chosen were of a widely different nature, but all are met with in practice. Corrosion in air in the open is common of course. Corrosion in dilute sulphuric acid is representative of corrosion in mineral acids, corrosion in sodium chloride solution is representative of corrosion in sea-water. Corrosion in ferric-sulphate is typical of corrosion in an oxidizing solution. Many methods of accelerated corrosion testing have been advocated, and at a recent meeting of the American Society of Testing Materials (42) a committee recommended four methods for further investigation.

In the present work comparison can be made between atmospheric tests, tests in still distilled water, and in moving distilled water. Further comparison can be made between specimens simply rotating in a corrosive medium, and those which in addition have a slight current imposed.

The atmospheric and still distilled water tests have

TABLE XI.

The corrosion of some typical steels in distilled water, dilute sulphuric acid, sodium chloride and ferric sulphate solution. Conditions: Time - 4 hours. Specimens rotated in 250-500 cc. solution at 100 R.P.M. Room Temperature.

Sample No.	Steel No.	WEIGHTS IN GRAMS. before IMMERSION	after	loss	Dimensions (a) in inches: diam.	length	AREA in sq. cm.	Loss in mg.per sq.cm. per yr.	Average loss	Deviation.
0	1	2	3	4	5	6	7	8	9	10
				Distilled water.						
T6	.18	49.9494	49.9361	0.0133	.499	1.97	21.17	1380		
T9	.18	50.3191	50.3075	0.0116	.499	1.97	21.17	1200	1290	± 90
47	.5	51.6113	51.6017	0.0096	.505	1.97	21.41	983		
48	.5	52.2065	52.1915	0.0150	.505	2.00	21.76	1508	1245	±263
S4	Cr-V	55.7767	55.7670	0.0097	.504	2.03	22.11	961		
S5	Cr-V	57.5528	57.5478	0.0050	.507	2.06	22.60	484	723	±239
				Dil. H_2SO_4.						
T2	.18	50.5748	50.4462	0.1286	.499	2.00	21.49	13120		
T3	.18	49.0538	48.9716	0.0822	.498	1.94	20.81	8640	10880	±2240
49	.5	49.7665	49.7302	0.0363	.500	1.94	20.91	3795		
410	.5	51.5735	51.5350	0.0385	.500	2.00	21.53	3915	3855	± 60
S6	Cr-V	54.9412	54.8700	0.0712	.500	2.00	21.75	7170		
S7	Cr-V	55.8634	55.7746	0.0888	.506	2.00	21.81	8920	8045	±875
X50	Cr-plate	51.4072	51.4059	0.0013	.501	2.00	21.58	132		
X51	Cr-plate	49.9756	49.9668	0.0088	.497	2.00	21.39	904	518	±386
				NaCl Solution.						
T4	.18	50.4810	50.4693	0.0117	.500	2.00	21.54	1190		
T11	.18	50.9817	50.9700	0.0117	.500	2.00	21.54	1190	1190	± 0
412	.5	51.9341	51.9232	0.0109	.495	2.00	21.31	1120		
413	.5	49.9724	49.9644	0.0080	.505	1.94	21.11	830	975	±145
S8	Cr-V	55.4669	55.4671	+0.0002	.501	2.00	21.58	0		
S9	Cr-V	58.3064	58.2886	0.0178	.505	2.13	23.09	1690	845	±845
X52	Cr-plate	51.5156	51.5156	0.0000	.502	2.03	21.98	0		
X53	Cr-plate	52.3131	52.3095	0.0036	.500	2.06	22.04	358	179	±179

already been discussed. The technique of the other two methods follows.

ROTATION TEST.

Samples of 0.18 per cent carbon, 0.5 per cent carbon, Cr-V steels and Cr plate steels prepared in the usual manner were suspended from the chucks of an electrolytic cabinet such as in used in analytical work. The samples were immersed in 250 c.c. - 300 c.c. of the corroding solution, and rotated at a predetermined rate, usually 100 revolutions per minute. That this simple test accelerates corrosion in distilled water is shown by a comparison of the data in Table II and XI.

ELECTROLYTIC TEST.

If in addition to the conditions just described, an electric current be imposed upon the system, farther acceleration will be obtained. From previous work (47) the most desirable current density to use was known. A current of 0.05 amperes was used, and this was obtained from storage batteries under a pressure of about 20 volts. The current density was maintained less than 0.25 amperes per sq. dm. Samples of 0.18 per cent carbon, 0.5 per cent carbon and Cr-V steels were tested. The data is given in Table XII. In Table XIII the results of all tests made on 0.18 per cent carbon, 0.5 per cent carbon, Cr-V steels and Cr plate are summarized.

DISCUSSION OF RESULTS OF THE ACCELERATED TESTS.

No differences in the nature of the corrosion could be noted between the simple rotation test and the electrolytic test for any of the solutions used. In the still dis-

TABLE XI. (continued).

1	2	3	4	5	6	7	8	9	10	11
				$Fe_2(SO_4)_3$ Solution.						
T7	.18	51.4973	50.2220	0.2753	.499	1.97	21.17	28490		
T8	.18	50.3400	49.4726	0.8674	.499	2.00	21.49	88400	58445	±29955
416	.5	51.6025	50.6450	0.9575	.502	1.97	21.31	98400		
419	.5	51.7329	50.6369	1.0960	.498	2.00	21.42	112000	105200	±6800
S10	Cr-V	57.4177	56.4550	0.9627	.508	2.00	21.90	96180		
S11	Cr-V	59.8452	58.8969	0.9483	.508	2.13	23.21	89500	92840	±3340
X54	Cr-plate	50.8068	50.8086	0.0000	.501	2.06	22.16	0		
X55	Cr-plate	52.3462	52.3450	0.0012	.501	2.03	21.88	120	60	± 60

TABLE XII.

The electroylic corrosion of some typical steels in dilute H_2SO_4, sodium chloride solution, and ferric sulphate solution; Conditions: Time - 4 hours. Specimens rotated in 250 cc. solution at 100 R.P.M. Current ±0.05 amp. Room temp.

SAMPLE No.	Steel No.	WEIGHTS IN GRAMS. before IMMERSION	after	loss	Dimensions in inches: Diam.	Length	Area in sq.cm (a)	Current density amp. per sq. dm.	Loss in mg. per sq.cm. per year.	Average loss mg. per sq.cm. per year.	Deviation.
					Dil. H_2SO_4.						
T10	.18	48.6082	48.2097	0.3985	.495	1.94	20.68	0.24	42260		
T12	.18	49.9173	49.6366	0.2807	.499	1.94	20.87	0.24	29420	35840	± 6420
420	.5	50.9208	50.6430	0.2778	.504	1.97	21.40	0.23	28310		
421	.5	51.2195	50.9390	0.2805	.505	1.97	21.41	0.23	28680	28495	± 185
S12	Cr-V	55.7626	55.4471	0.3155	.504	2.03	22.11	0.23	31220		
S13	Cr-V	57.5421	57.2440	0.2981	.507	2.06	22.48	0.22	29060	30140	± 1080
					NaCl Solution.						
T51	.18	51.0056	50.7955	0.2101	.500	2.00	21.53	0.23	21360		
T52	.18	50.9170	50.7072	0.2098	.500	2.00	21.53	0.23	21310	21335	± 25
411	.5	50.7672	50.5439	0.2233	.499	1.94	20.87	0.24	23420		
417	.5	52.9226	52.6986	0.2240	.499	2.03	21.90	0.23	22390	22905	± 515
S14	Cr-V	55.4608	55.2206	0.2402	.500	2.00	21.53	0.23	24420		
S15	Cr-V	55.2823	55.0311	0.2512	.504	2.13	23.01	0.22	23890	24155	± 265
					$Fe_2(SO_4)_3$ Solution.						
T53	.18	51.0362	49.9452	1.0910	.499	2.06	22.08	0.23	108400		
T54	.18	50.7702	49.6950	1.0752	.499	2.03	21.90	0.23	107520	107960	±440
414	.5	52.1917	51.1068	1.0849	.505	2.00	21.76	0.23	109200		
415	.5	52.1555	50.9983	1.1572	.505	2.00	21.76	0.23	116490	112845	±3645
S16	Cr-V	54.8632	53.7404	1.1228	.505	2.00	21.76	0.23	113100		
S17	Cr-V	55.7675	54.4809	1.2866	.505	2.00	21.76	0.23	129400	121250	±8150

(a) One end of each specimen was paraffined. **NOTE:** For analyses of solutions used see TABLE V.

TABLE XIII.

Comparison of results from various methods of testing samples in several corrosive media. Average losses and deviations given in milligrams per sq. cm. per year. Speed of rotation for all rotation tests, 100 R.P.M. This table compiled from tables given previously.

Method of Testing & Solution.	0.18 per cent C. average	0.18 per cent C. deviation	0.5 per cent C. average	0.5 per cent C. deviation.	Cr-V steel average	Cr-V steel deviation	Cr-plate average	Cr-plate deviation.	Time[a]
1	2	3	4	5	6	7	8	9	10
Atmospheric	1192	± 8	845	± 28	68	-	1.10	.70	1125 hrs.[b]
Still dist. H_2O	92	approx. ± 3	84	approx. ± 3	53	± 3	21	approx. ± 20	504 hrs.
Rotated in dist. H_2O.	1290	±90	1245	±263	723	±239	-	-	4 hrs.
Rotated in dil. H_2SO_4.	10880	±2240	3855	± 60	8045	±875	518	±386	"
Rotated & accelerated electrolytically in dil. H_2SO_4.	35840	± 6420	28495	± 185	30140	± 1080	-	-	"
Rotated in NaCl sol.	1190	± 0	975	± 145	845	± 845	179	± 179	"
Rotated and accelerated electrolytically in NaCl sol.	21335	± 25	22905	±515	24155	± 265	-	-	"

(a) Time period exposed from which average was calculated.
(b) The Cr-V steel was exposed 957 hours.

TABLE XIII (continued).

1	2	3	4	5	6	7	8	9	10
Rotated in $Fe_2(SO_4)_3$ solution.	58445	± 29955	105200	± 6800	92840	± 3340	60	± 60	4 hrs.
Rotated and accelerated electrolytically in $Fe_2(SO_4)_3$ solution.	107960	± 440	112845	± 3645	121250	± 8150	-	-	4 hrs.

tilled water test there was opportunity for a colloidal coating to form and adhere. It might appear that this coating retarded the corrosion rate in the case of still distilled water as compared with the rotation test, but the difference in time exposed is a factor which can not be directly equated.

Consider the corrosion of 0.18 per cent carbon steel in dilute H_2SO_4, NaCl solution and $Fe_2(SO_4)_3$ solution in the simple rotation and electrolytically accelerated tests. In sulphuric acid the acceleration obtained by the use of the electric current is about 3.5 times. In NaCl solution it is nearly 20 times. In ferric sulphate solution the deviation is so great that not even an approximate increase can be given. The ratio of the acceleration is of the same general order of magnitude for the other steels, but no conversion factors can be definitely stated. R. E. Hall (a) of the U. S. Bureau of Mines has intimated that he believes that the chief value of

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(a) Private communication, and Bulletin 15, Coal Mining Investigations. Carnegie Institute of Technology. (In Press)

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the electrolytic test lies in determining the nature of the corrosive attack rather than in determining the rate of corrosion which mibht be expected in service, even if the test be made in exactly the same corrosive medium as used in service conditions. R. J. Anderson, J. R. Adams, and the writer (47) have found good agreement between the results of long-time tests and the accelerated electrolytic test in the case of mine waters.

There is no one general accelerated test which can be

used under all conditions. Special tests to meet the requirements of the varying conditions will probably continue to be used. In this connection the results of the work of Committee B-3 of the A.S.T.M. may throw more light upon the subject.

SUMMARY AND CONCLUSIONS.

1. A review of the theories of corrosion which have been advanced shows that no one theory of corrosion will account for all observed cases of corrosion, and in other ways the theories are inadequate, at least as they are usually explained.

2. In order to simplify a consideration of the initiation and progress of corrosion in general, the writer applied the modern conceptions of the nature of the atom to the problem, and shows that all corrosion inception and progress can be considered as entirely a process of oxidation, if oxidation be defined as the loss of electrons from the corroded metal.

3. CORROSION and CORROSION RATE are differentiated as follows: Corrosion refers to the nature of the change of state in the metal as the oxidation occurs - that is, to the evidences of chemical and physical change. Corrosion rate refers to the magnitude of the change of state per unit of time, and is usually expressed as the average loss in weight per unit of time. Of course the true rate at any moment is not necessarily the same as this average.

4. The following factors affecting the corrosion rate and nature of corrosion are discussed: (a) Chemical composition

of the metal or alloy; (b) the physical condition of the metal or alloy; (c) the chemical composition and concentration of the corroding medium; (d) the physical constitution of the corroding medium; (e) the velocity of the corroding medium, or the velocity of the metal in the medium; (f) the effect of time of exposure to the corroding medium upon the nature of the corrosion and the rate; (g) the effect of temperature of the corroding medium (or the metal) upon the rate and nature of corrosion; (h) the solution pressure of the metal or alloy; (i) electrical conditions of immersion which might affect the rate of corrosion; (j) the effect of the formation of films and coatings upon subsequent corrosion and corrosion rate; and (k) the effect of light upon the nature and rate of corrosion.

5. Experimental work was done to determine the effects of some of the factors mentioned above, and results may be summarized as follows:

A series of steels of different carbon percentages, and samples of alloy steels, and of samples protected by plating with chromium or iron-chromium alloy were exposed to the action of the atmosphere and distilled water. All factors were maintained as near constant as possible, or at least had equal opportunity to act upon the specimens. As the carbon varied from steel to steel, the chemical composition may be considered to be the factor examined. The following results were determined:

(a) There was no difference in corrosion rate which could be traced to the carbon content. The Cr-V steel, the Ni-Si steel, and the plated samples all showed considerable

resistance to the attack of the atmosphere and to the attack of distilled water.

(b) In air and distilled water, the corrosion rate is high at the initiation of the corrosion and for a short time thereafter. The rate then diminishes, falls to a minimum and then slowly increases. For the conditions of the test then (several steels in air and distilled water) the time factor is a very important one.

(c) Samples of a typical steel were corroded in still distilled water and in dilute H_2SO_4 at different temperatures between room temperature and the boiling points. At the lower temperatures the rate of change per degree rise in temperature is very small, but this increases rapidly near the boiling point.

(d) Small quantities of gelatine markedly retard the corrosion rate in distilled water and in dilute sulphuric acid.

6. The effect of light upon the corrosion rate is a minor factor. Nevertheless, various kinds of light change the rate of corrosion. Thus ultra-violet light markedly increases the corrosion rate in air and in distilled water. For short time periods the effect of darkness is not noticeable. Red light was also used and seemed to accelerate the rate slightly but this was not fully confirmed.

7. Methods of testing metals for corrosion resistance are briefly discussed and those used in the present investigation were described and compared. Tests were made in the atmosphere, in still distilled water, and in several solutions

in which the specimen was rotated. The accelerated electrolytic test was also used. For an investigation of this kind no one method would be superior to another, and there is no single method of corrosion testing universally applicable in testing metals and alloys for corrosion resistance prior to placing them in actual service. Each case is a problem in itself. The simple rotation test and the accelerated electrolytic test, however, are widely applicable.

8. No metals were corroded to failure, and the results are applicable only when considering corrosion in its initial or early stages.

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SUPPLEMENT

NOTES ON THE PLATING OF CHROMIUM ON STEEL.

By

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Introduction.

In studying the literature dealing with the fundamental factors in corrosion processes, also in laboratory investigations, it became increasingly evident that by far the most important factor is that of the chemical composition of the metal or alloy. The results of the investigation of the effects of the various factors upon the nature and rate of corrosion have been reported elsewhere.(27) a In that investigation tests were made upon a variety of steels, and steel samples upon which chromium and chromium-iron alloy had been plated were also included. It is the purpose of this paper to discuss briefly the technique of chromium-plating, and to note the results of some attempts to bring about the cementation of chromium-plated steels.

(a) Numbers refer to bibliography.

HISTORICAL REVIEW.

It has long been realized that articles plated with chromium would probably be very resistant to corrosion and would have other desirable properties, including a silver-like luster when buffed. A review of the literature might lead one to suppose that the problem of chromium-plating had in general, been solved successfully. At the present time, however, chromium-plating is not done commercially as far as the writer is aware. The resistance to corrosion of chromium-plated articles has been studied but not in great detail.

Bunsen (1) seems to have been the first to attempt chromium-plating. He obtained metallic chromium in brittle sheets from a bath of chromous and chromic chlorides.

The patents of Place and Bonnet (33, 34, 35, 36) made great claims, but investigation (31) proved them to be worthless.

Feree (10) obtained fairly pure chromium by electrolysis of chromic chloride (740 gr. H_2O, 100 gr. HCl, and 160 gr. crystallized chromic chloride). He also obtained a silver-white precipitate from chromium and potassium chlorides. In each case the current density used was 0.15 amp. per sq. cm., with a tension of 8 volts. (cf. Le Blanc (31).)

Cowper-Coles (6) also succeeded in producing chromium from an aqueous solution of chromic chloride. He used a current density of 40-50 amp. per sq. ft., and electrolyzed at 75° C.

Newman and Glaser[11] studied the influences of current density, concentration, and temperature of different solutions. They obtained good deposits from chromic-chloride solutions at temperatures up to 50° C.

Diaphragm cells were used in many of the early investigations.

Carveth and Mott[12] and Carveth and Curry[13] made important advances in this work. The two former investigators found that the presence of a chromous salt was essential for the successful deposition of the metal from a sulphate or chloride solution, and that temperature has quite an effect upon the quality of the deposit and on the efficiency of the operation. Carveth and Curry found that the addition of sulphuric acid to a chromic-acid bath had a beneficial effect.

The work of Sargent[17] is noteworthy. He concludes that a chromic-acid solution containing a small quantity of chromic sulphate is the most promising for the electro-deposition of chromium. He obtained deposits up to 1/2 inch in thickness, plating from solutions of this type. He also noted the resistance of the chromium to corrosion.

Salkover [23] investigated many different baths and concludes as follows:-

> Uniformly good results can be obtained from a bath containing 30 per cent CrO_3 and 1 per cent $Cr_2(SO_4)_3$. The cathode current density should be from 0.8 to 1 amp. per sq. in. The CrO_3 content may become considerably impoverished without harmful results, also a somewhat higher concentration of the sulphate is permissible. Room temperature alone is needed. The use of two anodes, with the cathode between, gives more uniform results.
>
> Most other chromium salts do not give results at all comparable in quality to those obtained by the use of the chromic acid-chromic sulphate solutions.

Liebreich [19,20,21] used low voltage and reduced chromic acid solution containing a little sulphuric acid, and from 100 gr. per liter to 1000 gr. per liter of chromic acid. The current density varied from 10 to 85 amp. per sq. dcm. He used iron, copper, nickel, and brass as electrodes.

The work of Schwartz [18] applied directly to the plating of chromium on steel. His conclusions are here quoted in full, since it is with the plating of chromium on steel that the present investigation is mainly concerned.

1. Good, adherent deposits of chromium on iron were obtained, using solutions containing 3 gr. per liter of chromium sulphate and from 200 to 400 gr. per liter of chromic acid.

2. The cathode current density range for good deposits was found to be from 9.3 to 16 amp. per sq. dcm. (100 to 150 amp. per sq. ft.).
3. Best results were obtained using Sargent's solution containing 3 gr. per liter of chromium sulphate, 245 gr. per liter of chromic acid, and a current density of 1.3 amp. per sq. dcm. (125 amp. per sq. ft.). The anodes used were chromium. The solution was at room temperature, and stirring, in addition to that caused by the evolution of hydrogen, was found unnecessary.
4. Chromium anodes in the above solution show no tendency to become passive even after long and continuous plating operations. Chromium anodes are cheaper than platinum and better than lead.
5. The simultaneous evolution of hydrogen, with chromium deposition on iron is essential to good results. The hydrogen appears to protect the freshly discharged metal and to counteract the great tendency of chromium to pass back to the chromous ion stage. This tendency is particularly marked in the strongly oxidizing medium of chromic acid.
6. Chromium-plated iron and steel have a hard, bright, silver-like surface.
7. Chromium-plated iron and steel resist atmospheric corrosion indefinitely.
8. Chromium-plated iron and steel are resistant to the action of fumes of nitric acid, hydrogen sulfide, and ammonia. They also resist the corrosive action of molten tin, zinc, and brass.
9. Steel does not lose its temper during chromium-plating.
10. Chromium-plated iron does not resist electrolytic corrosion in mineral acids.

Rengering (24) investigated chromium plating-baths, using brass sheets and copper "electrotypes" as cathodes, and anodes of lead and chromium. He concluded that ---

> --- there is no difference in the quality of the plates produced by baths using lead anodes and those using chromium anodes. --- chromic acid baths cannot operate with continuously good results at temperatures above 17° C. --- heavy deposits of pure chromium cannot be plated without granulation taking place, that chromium deposits heavier than flash coats must be alloyed with a binding agent to prevent granulation, and that nickel is a suitable binding agent for use in depositing heavy plates (0.001 inch or more) of chromium.

There is no question but that on electrolyzing the chromic acid-sulphate bath such has been found to be the most suitable for use, the temperature rises appreciably. If the plating bath be cooled in ice water much better results are obtained. In the present work the method employed by Schwartz was followed, with the difference that the plating bath was kept cool in running water. For the purpose for which the plated specimens were desired, cooling by means of an ice bath was not necessary, although it was necessary to cool the solutions somewhat.

EXPERIMENTS IN PLATING CHROMIUM ON STEEL.

Either cast chromium in fairly large pieces, 3.81 by 2.54 by 10.16 centimeters (1.5 by 1.0 by 4.0 inches), or a number of smaller pieces hung in a basket made of aluminum wire, were used as anodes. The pieces of mild steel used were cylinders approximately 5.1 centimeters (2 inches) long by 12.7 centimeters (1/2 inch) in diameter. A number was

stamped in one end, and an aluminum or copper wire was attached to the other, either by means of solder in the case of copper, or by drilling a small hole, inserting the aluminum wire, and then swaging the steel around the wire. The wires later served as a means of hanging the specimens in corrosion tests.

The bath used consisted of 3 gr. of chromium sulphate, 245 gr. of chromic acid, and 5 c.c. of concentrated H_2SO_4 per liter of water (essentially Sargent's solution). The current density used was 3.77 amps. per sq. dcm. (350 amp. per sq. ft.). The steel specimens were hung from a bus-bar in the middle of the battery jar, and two anodes were used. The temperature was not allowed to exceed 24° C., The weight of chromium deposited over the area of each test piece (average area 22.8 dcm.) varied, for a plating time of 1 hour, from 0.2 to 0.3 gr. The probable depth of plate then, varied from 0.00127 cm. (0.00049 inches) to 0.00193 cm. (0.00072 inches) assuming the plated chromium to have a specific gravity of 6.9 Microscopic examination of a cross section confirmed this depth of plate approximately.

Alloys of chromium and iron were plated on steel and the specimens included in the corrosion and other tests. The method of plating these alloys is reserved for another paper.

The ever-increasing use of steels of the "stainless" type and of alloys of iron, carbon and chromium in general,

as materials resistant to a large variety of corrosive media including the atmosphere and natural waters, had led to the developement of many varieties of chromium irons and steels. Schwartz (18) as well as the writer (27) has shown that chromium-plated steels are quite resistant to many corrosive media.

Kelly (26) has described the process of chromizing, and gives the following conditions as necessary for the production of a chromized surface: (1) Chromium of at least 95 per cent purity; (2) powdered Al_2O_3 as a diluting agent; (3) pure hydrogen free from moisture and oxygen; and (4), a furnace that will operate at 1300° C., or higher in an atmosphere of hydrogen. He further notes that the chromium must be in intimate contact with the iron, and that the iron or steel must have a low carbon content. He found that chromized iron was resistant to corrosion (salt spray test) and to the attack of HNO_3, but not to the attack of H_2SO_4 and HCl; also that the chromized surface is soft but may be case-hardened, yet if case-hardened the material is less resistant to corrosion.

Charpy (25) found that Cr adsorbs CO, but more slowly than Mn, and that Cr_2O_3 and C are formed. In iron containing Cr, the Cr is oxidized to Cr_2O_3 in the presence of CO, and a portion of the C liberated is taken up by the Fe. These of course are high-temperature reactions.

Consideration of the work of Kelley and Charpy led the writer to undertake a series of experiments to determine whether a process of plating and heat-treating could be worked out which would furnish a steel with a surface of iron high

in chromium content and hard enough to stand wear, and still be resistant to corrosion. Three general lines of procedure were employed as follows:

1. Plate the specimen with chromium and then attempt to case-harden through the chromium, followed by suitable heat-treatment.

2. Case-harden, then plate with chromium and then heat-treat.

3. Plate with chromium, heat-treat, and case-harden.

The steel used for test contained 0.18 per cent carbon, and the specimens were 2 inches long by 1/2 inch in diameter. The surface of the specimens was freed from scale but not brilliantly polished. No attempt was made to heat in hydrogen or to secure a higher temperature than was obtainable in the ordinary furnaces in the laboratory. The periods of treatment were kept short also, In other words, only relatively quick, inexpensive, commercial methods of treatment were employed.

Tables I, II and III summarize a series of experiments following the above outline. The chromium plates were plated as previously described. Where it seemed advisable, micro-structures were examined. None of the samples showed sufficient hardness and evidence of chromium diffusion to warrant preparing samples for a corrosion test. Many other tests not included in the tables were made with similar results. The tests reported in the tables were made using gas furnaces. Constant checks on change of hardness were made

TABLE I.

Data on the chromium-plating, heat-treating, and case-hardening of mild steel. (original scleroscope hardness 32-35).

Sequence of operations - (1) plate, (2) case-harden, and (3) heat-treat.

Sample No.	Time of plating in hours	Time and method of case-hardening.	Heat treatment.	Final scleroscope hardness	Remarks.
12	1	1 hr., pack.	c.w.f.	23	
13	1	1 hr., pack.	H_2O q.	37	slight exfoliation.
14	1	2 hr., pack.	1 hr. an., air cool, scl. 22. 1/2 hr. at 950°C., & H_2O q.	37	some peeling.
15	1	2 hr., pack.	2 hr. an., air cool, scl. 25, hr. an. & H_2O q.	30	bad exfoliation.
17	1	1 hr., pack.	2 hr. an., in Pb bath at 620°C., c.w.f.	20	surface blisters.
18	1	1 hr., pack.	3 hr. an. in Pb bath at 620°C., c.w.f.in g.f. from 620°C.	25	surface blisters.
121	1	1/2 hr. cyanide.	1 hr. an., & oil q. scl. 25 surface good, 1/2 hr. an. & H_2O q.	27	surface fair, but no evidence of Cr.

ABREVIATIONS USED: hr=hours, c.h.=case-harden, pl=plate, q=quenched, c.w.f.=cooled with furnace, g.f.=gas furnace, an=annealed at temperature of 950-1050°C., scl=average scleroscope reading, oil q.=oil quench in oil at 250°C

TABLE II.

Data on the chromium-plating, heat-treating, and case-hardening of mild steel. (original scleroscope hardness 32-35).

Sequence of operations - (1) case-harden, (2) plate, and (3) heat-treat.

Sample No.	Time of plating in hours:	Time and method of case-hardening:	Heat treatment.	Final scleroscope hardness	Remarks.
110	1 hr., pack.	1	1 hr. an., c.w.f.	22	Badly exfoliated.
111	1 hr., pack.	1	2 hr. an., c.w.f.	19	Badly exfoliated.
112	1 hr., pack.	2	2 hr. an., c.w.f.	20	Badly exfoliated.
113	2 hr., pack.	1	1 hr. an., c.w.f. scl. 35, good surface, 1/2 hr. an., H_2O q.	67	Regular case-hardened structure, but plate not continuous.
114	1 hr., pack.	2	1 hr. an., in Pb. bath at 620°C., c.w.f. in g.f. from 620°C.	25	Surface blisters.
122	1/2 hr. cyanide.	1	1 hr. an., oil q. scl. 25, surface fair, 1/2 hr. an., & H_2O q.	35	Fair surface.

ABBREVIATIONS USED: hr-hours, c.h. case-harden, pl-plate, q=quenched, c.w.f.= cooled with furnace, g.f.=gas furnace, an=annealed at temperature of 950-1050°C., scl=average scleroscope reading, oil q.=oil quench in oil at 250°C.

TABLE III.

Data on the chromium-plating, heat-treating, and case-hardening of mild steel. (original scleroscope hardness, 32-35).
Sequence of operations - (1) plate, (2) heat-treat, and (3) case-harden.

Sample No.	Time of plating in hours	Heat treatment.	Time and method of case-hardening	Final scleroscope hardness	Remarks.
16	1	1 hr. an., c.w.f.	None.	30	Bad exfoliation.
116	1	1 hr. an., air cool, scl. 20.	1 hr. pack c.w.f.	32	Some scaling.
117	2	2 hr. an., air cool, scl. 20.	1 hr. pack c.w.f.	35	Some scaling.
118	1	1 hr. an., air cool, scl. 20.	2 hr. pack c.w.f.	35	Slight exfoliation.
119	1	2 hr. an., air cool.	2 hr. pack & H_2O q.	22	Bad exfoliation.
123	1	1 hr. an., air cool, scl. 20.	1 hr. pack air cool, 1 hr. an., & oil q.	20	Fair surface.

ABBREVIATIONS USED: hr-hours, c.h.=case-harden, pl=plate, q=quenched, c.w.f.=cooled with furnace, g.f.=gas furnace, an=annealed at temperature of 950-1050°C., scl=average scleroscope reading, oil q.=oil quench in oil at 250°C.

with the scleroscope, and are also noted in the tables.

Tests similar to those run in the gas furnace were run in a small electric furnace where a slightly greater temperature was obtained. The period was extended to 6 hours to allow a better chance for diffusion. In no case did the hardness of the specimen materially increase where the specimen had been chromium plated either before heat-treatment for diffusion or case-hardening treatments. This leads to the conclusion that at ordinary case-hardening temperatures, chromium as plated does not absorb carbon, - that is, it is not cemented at least to any appreciable extent. Cast chromium can be readily made to take up carbon at the ordinary case-hardening temperature. Small pieces of cast chromium were weighed, packed in carbonizing material and case-hardened at about 900° C., for one hour. They showed a gain in weight of 0.25 per cent and were insoluble in any ordinary mineral acid or combination of acids.

SUMMARY AND CONCLUSIONS.

Steel can be chromium-plated by the methods described by Schwartz, but it is recommended that the temperature of the solution be kept low.

For periods up to 6 hours, and temperatures up to 1050° C., no combination of chromium-plating, heat-treating for diffusion, and case-hardening could be found that would give surfaces which were hard and at the same time in such physical shape as to make it likely that they would resist corrosive media.

Chromium plate on steel prevents cementation for the ordinary time and temperature conditions employed in case-hardening.

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