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CORROSION REDUCTION BY CATHODIC PROTECTION

By

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Chapter I - Introduction and summary

Purpose of investigation

The purpose of this investigation is to determine the amount of cathodic protection afforded drawn steel oil well casing at the expense of anodic solubility of the drawn steel tubing. The use of cast iron and galvanized steel tubing was investigated to determine if their rates of anodic solubility would be less than that of the drawn steel tubing. The effect of three different brines on the rate of corrosion was found. Quantitative tests were made on the comparative rates of corrosion of neutral, anodic, and cathodic cold rolled steel strips by determination of their weight losses. The minimum current density necessary to give cathodic protection was determined. Tests were made on the relative amounts of corrosion by continuous and intermittent immersion. The effect of removal of gases dissolved in the brine on the amount of corrosion of steel strip samples was investigated. Consideration is given to the commercial feasibility of cathodic protection

of both casing and tubing by means of an intermediate anodic pipe. This third electrode may be maintained anodic to both casing and tubing either by means of applied potential or by the use of metal electropositive to casing and tubing. Since iron oxide is electropositive to metallic iron, this third electrode may consist of a pipe with iron oxide surface, i.e., a rusty iron pipe.

Corrosion of oil well casing and tubing

Due to its different causes, separate consideration should be given to corrosion of the portion of the casing and tubing which comes in contact with the brine and that above the maximum level of the brine.

Corrosion by brine

Most Illinois oil wells are pumped for a limited period during each 24 hours, the length of the pumping period depending on the volume of the liquid produced. Many wells produce large amounts of salt water with the oil and require relatively long

pumping periods, whereas for others as little as 1/2 hour's pumping per day is sufficient. Between periods of pumping, the liquid level rises in the wells to as much as 200 feet. The pumping removes the liquid, thereby leaving this portion of the surface of both casing and tubing wet with brine and exposed to corrosive gases if present. Therefore, each day this portion of both casing and tubing are subjected alternately to immersion in the brine and to drying.

The rate of corrosion of this portion of both inside and outside surfaces of the tubing, and inside surface of the casing is accelerated by this set of conditions. However, the outside surface of the casing is not normally subjected to accelerated corrosion. Instead, it is usually continuously wet by ground water which is not free to circulate. Thus this portion of the casing tends to corrode from the inside out, thereby permitting water to enter the well from strata higher than the producing sand. This necessitates either the insertion of a packer to prevent the water from entering the well, or the pulling of the casing to replace

the defective sections. The latter method is more satisfactory, although it is expensive. As contrasted to this, the removal and replacement of corroded tubing is relatively inexpensive.

Corrosion of iron in a brine is due to electrolysis. By definition, electrolysis is the flow of current through a conducting liquid between two electrodes; the positive and negative electrode being referred to as anode and cathode, respectively. If the electrodes are composed of an electrochemically soluble metal, such as iron, the passage of current causes the anode to dissolve and tends to deposit metallic ions on the cathode. This dissolving of the anode is corrosion.

Drawn steel, such as tubing and casing, has areas which are anodic with respect to the remainder of the surface. When such iron is immersed in brine, a battery action sets up currents between anodic and cathodic areas. This results in corrosion located at anodic areas. In such corrosion of iron, the dissolved ferric ion combines with oxygen, which is liberated at the anode, to form iron oxide, commonly known as rust. This iron oxide naturally

deposits on the anodic area where it is formed.

Normally the iron oxide is even more anodic than the original anodic area in the iron. The resultant concentration of corrosion tends to form a pit in the iron surface. Furthermore the process of corrosion causes an increase of the hydrogen ion concentration of the brine within the pit and, also, there is a tendency for the confinement of the anodically liberated oxygen within the pit. Both these factors increase the rate of corrosion, especially at the bottom of the pit, and thereby tend to form a deep narrow pit.

Corrosion by gases

In certain Illinois oil pools, a large amount of sulfur is present in the form of hydrogen sulfide, which is liberated as a gas. This hydrogen sulfide will tend to dissolve in the moisture film which normally covers the surface of the casing and tubing above liquid level. In the absence of sufficient oxygen, the

hydrogen sulfide will corrode the iron pipe at anodic areas with the electrolytic deposition of iron sulfide and sulfur on these areas. Both these products are cathodic to iron and therefore tend to limit the spread of corrosion. But in the presence of sufficient oxygen the hydrogen sulfide may be converted to sulfuric acid, which will corrode the iron pipe at anodic areas with the electrolytic deposition of iron oxide which is anodic to iron and, therefore, tends to accelerate corrosion with resultant pitting.

Since such a pipe surface is merely covered by a corrosive film rather than being immersed in an electrolyte, it cannot be protected from corrosion by means of a second anodic electrode.

Summary

This report records the results of tests made on the rate of corrosion of drawn steel casing and tubing; cast iron and galvanized steel tubing, and cold rolled steel strip in oil well brines under neutral, anodic, and cathodic conditions. It also presents the electrolytic theory of corrosion, and a brief review

of various methods of corrosion protection.

It was found that the life of cathodically protected casing may be increased at the expense of a shortened life for the anodic tubing. Cast iron and galvanized steel tubing proved to be unsatisfactory as an anode; the former having a greater susceptibility to pitting, and the latter having a faster rate of anodic solubility.

Corrosion was found to be more rapid in some brines than in others. Cathodic protection, however, was given in all the brines tested.

The loss in weight of cold rolled steel strip samples corroded under carefully controlled conditions, was reproducible to within one-tenth of one per cent of their original weights.

Samples which were continuously immersed in the brine were found to corrode more slowly than those intermittently immersed, both with and without potential applied for cathodic protection. Nevertheless, cathodic protection gave approximately the same fold increase in life for both contiuous and intermittent immersion.

The minimum current density required to give complete cathodic protedtion in the most corrosive brine tested was found to be about 0.23 milliamperes per sq. in., which is equivalent to about 33 milliamperes per square foot. Under these conditions, cathodic strip samples showed no loss in weight although the current resulted in a 5.5 fold increase in anodic corrosion.

Removal of air and other gases dissolved in the brine greatly reduced the rate of corrosion of a sample.

Although applied potential may be used in field practice to protect the cathodic casing at the expense of the anodic tubing, nevertheless it seems doubtful if such a procedure would be economically feasible. But in certain instances where corrosion takes place primarily on the surfaces of the casing and tubing during the periods they are submerged in the brine, it seems that it may prove feasible to protect both casing and tubing surfaces by the introduction of an intermediate rusty iron pipe which would be electropositive, due to its iron oxide surface, to both casing and tubing.

Acknowledgments

Appreciation is expressed for the assistance of Mr. J. K. Kerr, Vice President of the Ohio Oil Company, who furnished samples of oil well brines and samples of casing and tubing stock.

After the experimental work in this investigation was completed, Mr. M. J. Kenefake of the Tidewater Oil Company furnished the information that he had previously made independent field tests on the use of an intermediate metal tubing in the form of a rusty iron pipe.

The tests were performed by Dr. J. J. Gibbons, of the Civil Works Administration, and Mr. H. C. Roberts, Physics Assistant of the Illinois State Geological Survey. The photomicrographs, photographs, and drawings were prepared by the latter.

Dr. A. H. Bell, Geologist and Head of the Oil and Gas Division of the Survey, contributed valuable suggestions.

Dr. M. M. Leighton, Chief of the Survey, has been helpful by his personal interest in the investigation.

Chapter II - Electrolytic theory of corrosion

The electrolytic theory of corrosion, which is now universally accepted, is based on the experimental fact that corrosion is caused by anodic solubility due to flow of electric current in an electrolyte. An electrolytic solution is dissociated into positive and negative ions which carry the electric current, the direction of current through the electrolyte being the direction of motion of the positive ions which move from the anode to the cathode.

Electric current may be passed through an electrolyte by either of two means.

Contact potential protection

The first method of passing a current through an electrolyte is by the means of two electrically connected pieces of metal which have different contact potentials. This results in the flow of positive ions from the electropositive metal to the relatively electronegative metal and the flow of negative ions through the electrolyte in the opposite direction; the circuit being completed

through an external electric conductor through which the direction of electronic flow is from anode to cathode. Corrosion is not normally caused by the presence of two dissimilar metals in an electrolyte, but rather by the presence of dissimilar areas on the surface of the same piece of metal. In the case of anodic and cathodic areas on the same piece of metal, the body of the metal itself acts as the return circuit for the electronic current.

Applied potential protection

The second method of passing current through an electrolyte is by the means of two pieces of similar metal maintained at different potentials by externally applied voltage. The metal connected to positive potential is anodic with respect to the metal connected to negative potential, the latter thereby being cathodic; and, likewise, the positive ions in the electrolyte move from anode to cathode. In both instances, the anode goes into solution, and the cathode is protected from corrosion.

Causes of difference in contact potentials

Different areas on the surface of a single piece of metal may have various contact differences of potential. Anodic areas are caused by impurities on the surface of the metal, by localized stresses, and also by temperature differences. Iron oxide is a common example of surface impurity. Since iron oxide is anodic to iron, a difference in potential will exist between a rusty area on a pipe and the adjacent metallic surface. Localized stresses are common in drawn steel pipe. The process of drawing results in longitudinal stresses and frequently a piece of drawn steel pipe will show grooves which have been corroded along the lines of stress. Temperature differences play a relatively unimportant part in corrosion of casing and tubing since the temperature gradient in the casing and tubing is usually small.

Faraday's discovery

In 1833 Faraday began a systematic investigation of the effects of electrolytic current. He found that the amount of a substance dissolved at the anode or deposited at the cathode is

proportional to the quantity of electricity. Thus, a greater magnitude of current results in a more rapid rate of loss of material at the anode. According to Ohm's law, the amount of current depends on the potential difference. Thus the more anodic an area, the greater will be the potential difference and, therefore, the more rapid the rate of corrosion. When a naturally anodic area is covered by an even more anodic product of corrosion such as iron oxide, then the rate of the localized corrosion is increased with resultant pitting.

Chapter III - Various methods of corrosion prevention

Many methods of preventing or minimizing corrosion have been used. They may be listed under two general classifications, electrolytic protection, and mechanical protection.

Electrolytic protection

Electrolytic protection refers to the reduction or elimination of the conditions necessary for electrolytic action of the brine on the piping. This may be secured by introduction of dissimilar metals as electrodes, by applied potential which maintains the piping in a cathodic state, by annealing the piping to remove stresses, by use of electronegative metals, or by electroplates which are anodic to the piping, thereby protecting the piping until the electroplate is completely dissolved.

Dissimilar metals. - Previous to the work of Faraday, Sir Humphrey Davy investigated the electrolytic effects at the anode and cathode of a galvanic cell. He discovered that there was a decomposition of the material of the electrode from which current

flows into the solution, but that at the other electrode the tendency was for material to be deposited, rather than removed. In 1807, working on this principle he obtained metallic potassium by electrolytic decomposition of caustic potash. On passing an electric current between two electrodes immersed in the potash, the metal was deposited on the cathode.

Davy suggested the first use of potential protection, applied to the copper sheathing of the bottom of a ship. His suggestion was to use iron protecting pieces, electrically connected to the copper, relying upon the galvanic effect of the iron-copper couple immersed in sea-water to protect the copper at the expense of the iron. At this time, no other method of obtaining such a potential difference was feasible.

In 1915, Cumberland demonstrated a process for protection of boiler tubes from corrosion by using zinc anodes electrically connected to the boiler walls. When properly spaced, these proved effective. The principal disadvantages were that too many electrodes

were required, and it was extremely difficult to space them so that protection for all parts of the boiler was obtained. Also variations in electrical conductivity of the boiler water proved troublesome.

Applied potentials. - In 1913, Clement and Walker of the U. S. Bureau of Mines, working on the problem of cathodic protection by applied potentials, made experimental determinations of the magnitude of current density necessary to prevent the corrosion of cathodic iron surfaces.

In 1918, Cumberland suggested a commercial application of cathodic protection by applied potentials to reduction of corrosion of boiler walls and tubes. He used a set of iron electrodes suitably insulated from the boiler walls and tubes. By applying external potential between the boiler and the electrodes, he made the former cathodic to the latter. Using this type of installation further protection has been obtained by adding salts of arsenic to the boiler water at intervals so that a protective coating of arsenic is plated out upon the cathodic boiler walls and tubes.

Since 1928, Kuhn, of the New Orleans Public Service, Inc., has made a noteworthy investigation of corrosion protection of gas and water mains which are subjected to the peculiarly corrosive conditions of New Orleans soils. He has been the pioneer in electrical drainage which consists of so electrically connecting the pipe lines to the trolley systems, that the pipe lines will be cathodic to the surrounding soil.

He has found that pipe lines which are kept cathodic to surrounding soil are much less subject to corrosion than before being so protected. On pipe lines which are too far outlying to be connected to trolley systems, he has applied a method of forced electrical drainage, in which the pipe line is maintained cathodic to the ground by the use of direct current from an automobile battery rectifier. For cathodic protection to be effective for more than one length of pipe, it is necessary for the sections of pipe to be welded to assure good electrical contact. This method of electrical drainage has proved itself both effective and economical.

In no instance did Kuhn find that a pipe, cathodic to its surroundings, was seriously affected by corrosion.

Annealing the piping to remove stresses. - The processes of pressing, rolling or drawing metals produce internal stresses. A normalizing treatment consists of heating the piping for a period of about 20 minutes above its softening temperature, followed by cooling in air. This process is a close analogue to that of annealing plate glass to remove its internal stresses.

Corrosion resisting metals. - Nickel, tin, lead, and copper have lower anodic solubilities than iron. Lead and copper tubing are the cheapest and most commonly used. Lead tubing lacks sufficient tensile strength to be used in oil wells, and copper tubing is far too expensive. Copper clad steel, however, is used with excellent results in pump barrels and valves.

Electroplates. - Zinc, cadmium, and chromium are the ordinary electroplates which are anodic to iron. Zinc is used most commonly; a zinc coating being known as galvanizing. A galvanized coating may be applied by electroplating or by hot dipping. A galvanized pipe

proves unsatisfactory in a brine because the extremely thin plate of anodic zinc is soon completely dissolved, thereby leaving the pipe unprotected.

Mechanical protection

In this report the expression, mechanical protection, is used to designate protection secured by an impervious layer of non-corrodible material which restrains the brine from coming in contact with the surface of the piping.

Non-metallic wrappings, paints, and cement coatings. - Tar soaked wrappings and asphalt paints have been used with excellent results on pipe lines, but such wrappings are impractical for use with oil well casings. Under usual conditions, it would not be necessary to use an asphalt coating on the outside of the casing, because the outside is not subject to severe corrosion. Also, asphalt coating is not suitable for the portion of the tubing and inside surface of the casing which come in contact with crude oil, because asphalt is oil soluble.

Although cement protected casing has not been used in Illinois, Mr. E. B. Cochran of the Hamilton Production Company has installed cement lined lead lines and tubing in a Bridgeport sand well in Lawrence County. He reports that on December 12, 1933, he put in cement lined lead lines known as Duroline which show no indication of corrosion to date, although the previous life of regular pipe was about one year. Also on April 9, 1936, he replaced the regular tubing with Duroline. Although it is too soon to report definite experimental results, Mr. Cochran expresses confidence that the tubing will be as satisfactory as the lead line unless the rod wears through the cement lining. The lengths of the Duroline tubing are connected with a special collar, having a central boss which extends even with the inside diameter of the cement lining. When the pipe is put together, a cement preparation furnished by the manufacturers of the pipe is mixed to the consistency of thick paint and applied to the inside of the collar and on the threads with a brush. The pipe, when screwed in, bucks against the boss thereby leaving a continuous cement lining in the joint.

Oxide and phosphate films. - The surface of a pipe may be protected by a film of the oxide or phosphate of the foundation metal. These films are formed by various proprietary processes such as the Bower-Barff, Gesuer, Wells, Dewees-Wood, Bradley, Bontempi, Buffington, Richards, Coslettizing, Parkerizing, and Spellerizing.

Passivifying treatment. - Certain metals in the iron group are known to possess both an active and a passive state. There is a divergence of opinion as to whether the passive state exists throughout the body of the metal or consists solely of an oxide surface-protecting film. Passivifying treatment consists in subjecting the metal to an oxidizing reagent such as concentrated sulfuric acid or chromic acid.

Chapter IV - Description of samples and procedure

Description of brines tested

Brines. - The samples of brine were obtained from three different wells, all belonging to the Ohio Oil Company. These were: Well No. 5, G. W. Jones farm. NW. cor. NE. 1/4 sec. 2, T. 5 N., R. 13 W.; Well No. 20, L. N. Tohill farm, NE. 1/4 NE. 1/4 sec. 31, T. 6 N., R. 11 W.; and Well No. 12, A. C. Vinsel farm, NW. 1/4 SW. 1/4 sec. 15, T. 5 N., R. 12 W., all in Crawford County. These brines were selected as representative of the most corrosive found in the State.

The samples of brine were collected at the casing head, placed in sealed metal cans, and brought to the laboratory. None of the brines, upon opening at the laboratory, contained enough sulfide gas to be detectible by odor. The chemical analyses of these brines are given in table 1.

Table I.

Analyses of brines used

Constituents	Tohill p.p.m.	Jones p.p.m.	Vinsel p.p.m.	Hypothetical combinations	Tohill p.p.m.	Jones p.p.m.	Vinsel p.p.m.
NH_4	5.1	10.3	5.8	$NaNO_3$	5.1	9.4	6.8
Na	4504.7	7023.2	5672.7	NaCl	10223.4	17076.0	11699.0
Ca	340.0	174.4	5.7	Na_2SO_4	1486.0	-	2090.0
Mg	220.0	93.9	52.8	Na_2CO_3	-	696.9	902.0
SiO_2	46.0	12.0	32.0	$(NH_4)_2SO_4$	18.5	-	-
N.V.M.	27.0	21.0	30.0	$(NH_4)_2CO_3$	-	27.3	15.4
Fe	1.6	6.0	6.0	$MgSO_4$	1089.2	-	-
Al_2O_3	9.0	1.0	5.0	$MgCO_3$	-	325.5	183.4
Mn	.4	Trace	.0	$CaSO_4$	646.5	-	-
SO_4	2346.0	.0	1414.0	$CaCO_3$	375.0	435.0	14. 0
Cl	6200.0	10372.0	7096.0	SiO_2	46.0	12.0	32.0
NO_3	3.5	7.1	5.3	Fe_2O_3	2.2	8.6	8.6
CO_3	-	-	360.0	Al_2O_3	9.0	1.0	5.0
HCO_3	457.5	1839.0	608.2	MnO	.5	Trace	-.0
Free CO_2 *	22.85	-	-	N.V.M.	27.0	21.0	30.0
H_2O *	1.0	2.6	2.3				
Total solids	14034.0	18782.0	15260.0	Total	13928.4	18612.7	14986.2

* Made in field.

Description of metals tested

Drawn steel casing and tubing. - The samples of drawn steel casing and tubing were cut from regular field stock in 6-inch lengths to facilitate handling. The casing and tubing were 6-inch and 2-inch inside diameter, respectively.

Cast iron and galvanized steel tubing. - The samples of cast iron and galvanized steel tubing were cut from new stock, obtained from the Inland Supply Company, 2-inch inside diameter, into 6-inch lengths.

Cold rolled steel strips. - The flat strip samples of cold rolled steel were 6-inch lengths cut from strip metal 1 1/2 inches wide by 1/16 inch thick. They were obtained from the Physical Plant Storeroom of the University of Illinois.

Procedure

Preparation of brines tested

Brines. - The surface films of oil were removed from the brines used with the pipe samples (casing and tubing). In addition to the removal of oil, the brines used with the steel strip samples were filtered to remove any suspended matter.

Preparation of metals tested

Pipes. - The samples of pipe were washed with water and brushed to remove all loose scale, thereby approximating the condition that exists when casing and tubing are installed in a well.

Cold rolled steel strips. - The steel strip samples, being new and clean, carried no scale. They were washed in alcohol to remove grease, and then in a bath of 85 per cent hydrochloric acid. This treatment resulted in a fresh surface by removing about 0.005 grams of metal from the sample. This was found more satisfactory than electrolytic cleaning.

Necessity for clean surfaces. - For reproducible determination of rate of corrosion by weight losses it was found necessary to use carefully cleaned surfaces. The steel strip samples were selected for these determinations. In order to duplicate field conditions, the pipe samples were not cleaned. Therefore the exact magnitude of weight losses on duplicate corrosion tests made on the pipe samples were not reproducible.

Photomicrographs

Samples of casing.- In order to obtain qualitative results on the rate of corrosion by the photomicrographic method, 6-inch lengths of casing were cut longitudinally into three samples of equal size. At the center of the convex surface of each of these samples, a small area, about 0.5 cm. square, was ground flat. This was given a high polish by grinding with successively finer grades of carborundum, polishing with french emery paper, and finishing with alumina.

These samples were then immersed in Tohill brine and corroded for various periods of time under neutral, anodic, and cathodic

conditions. They were then removed from the brine, washed in water, the polished spots lightly brushed with lens paper, and photographed. In each case the magnification used was 300 diameters.

A Leitz Ultrapak microscope was used with oblique reflected light, thereby reversing the light and shadow. Therefore the illustrations show the negatives of the photomicrographs to correspond to visual observation.

Samples of steel strips. - The photomicrographs of the steel strip samples were made with vertical illumination, using a d.c. carbon arc except for the photomicrograph of the pits which was made with both vertical and oblique illumination simultaneously. This was found necessary in order to give satisfactory reproduction of the pits. The intensity of the oblique illumination (incident at 45 degrees) was approximately 75 per cent of the total illumination.

Quantitative method of testing

Samples of pipe. - The samples of pipe were identified by center punch markes. Earthenware jars, eight inches inside diameter by ten

inches deep, were used as brine containers. After weighing, a pair of casing and tubing samples was placed coaxially in each jar. Battery clips on brightened spots on the pipes were used for the electrical connections. An air jet was placed in each jar to provide means for daily aeration. Wire markers in the jars indicated the original level of the brines so that distilled water might be added as required to replace evaporation losses. The group of samples used for intermittent immersion tests were removed from the brine for about eight hours daily and allowed to dry. The purpose of this, together with the daily aeration period of one hour, was to reproduce field conditions.

During the tests the currents were carefully checked with a milliammeter. At the conclusion of each test, the samples were removed from the jars, carefully wiped to remove loose rust, dried, and weighed.

Samples of cold rolled steel strip. - Each of the steel strip samples was identified by a number stamped on one end. Also a small hole was drilled by which a tight electrical connection could be made.

The containers for the brine were 600 cc. beakers. These were arranged in three parallel lines with nine beakers in each line. Three hangers were constructed so that all the samples in each line could be removed simultaneously from the brine. All the samples in each line were connected in series along with a variable resistance; the three lines were connected in parallel, and potential applied from a ten-volt storage battery as shown in figure 1.

The amount of current in each line was checked daily by a milliammeter and maintained very closely to the selected value. The precipitate which formed in the brine was removed periodically by filtration. All the samples in each line for intermittent immersion tests were removed simultaneously from the brine for their daily period of drying by lifting the hanger from which they were suspended. Distilled water was added as required to each beaker to replace evaporation losses. Before weighing the samples, at suitable intervals, they were cleaned by washing in water, then in 85 per cent hydrochloric acid, and then in alcohol to facilitate drying.

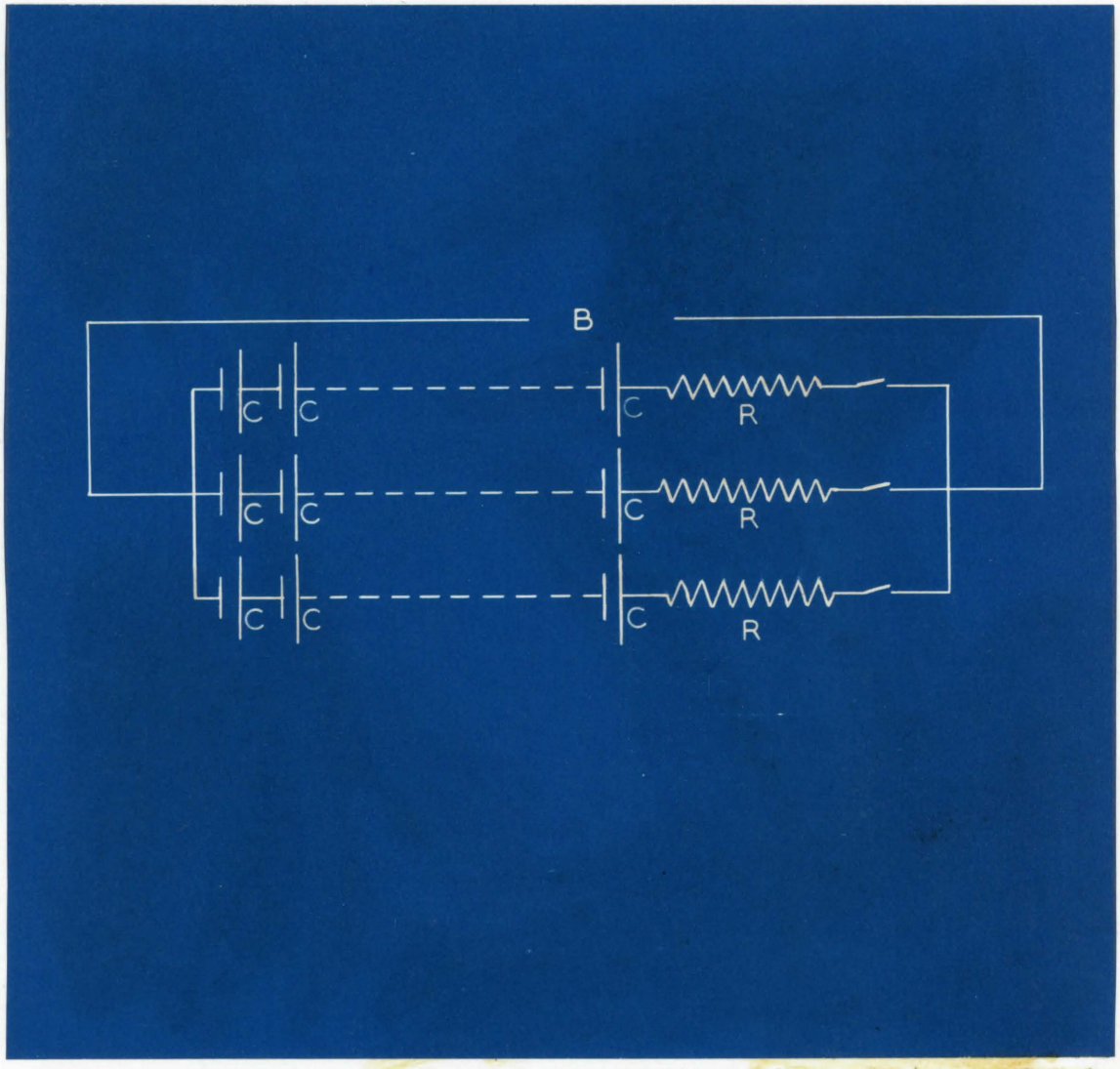


Figure 1 - Electrical Hook-up.

In order to test the effect of oxygen (air) in the brine upon the rate of corrosion due to immersion without applied potential, a pair of brine samples was prepared alike in every respect except as to the presence of air. The gases in the brine in each beaker were expelled by boiling. Then a strip sample was placed in the brine in one beaker and the surface of the brine immediately sealed over with wax to exclude air. The other brine was agitated when cool to entrap air, and left exposed to air. Distilled water was added to the latter as required to replace loss from evaporation.

Two strip samples were prepared for a microscopic study of the uniformity of corrosion over their surfaces, one for use as a cathode and the other as an anode. Cross hatched lines of paraffin were painted on the surface of each sample to provide non-corroded lines between the corroded squares. The microscopic depth of corrosion of various areas was determined with respect to that of the non-corroded areas.

Chapter V. - Results and discussion

Pipe samples

Qualitative comparison of rates of corrosion as determined by photomicrographs

Without applied potential

Figure 2 is a set of six photomicrographs which show various stages of corrosion of a polished surface of casing. Photomicrograph A shows the polished surface before immersion in the Tohill brine, B shows the surface after it had been corroded for 1 minute, C for 2.5 minutes, D for 10 minutes, E for 30 minutes, and F for 17 hours. An inspection of the figure shows an increase in the degree of corrosion with time, with definite indication of corrosion for an interval as short as one minute.

With applied potential

Cathodic potential. - Figure 3 is a set of eight photomicrographs which show various stages of corrosion protection of a polished surface of casing, due to a cathodic current density of 1.2 ma. per sq. in. Photomicrograph A shows the polished surface before immersion

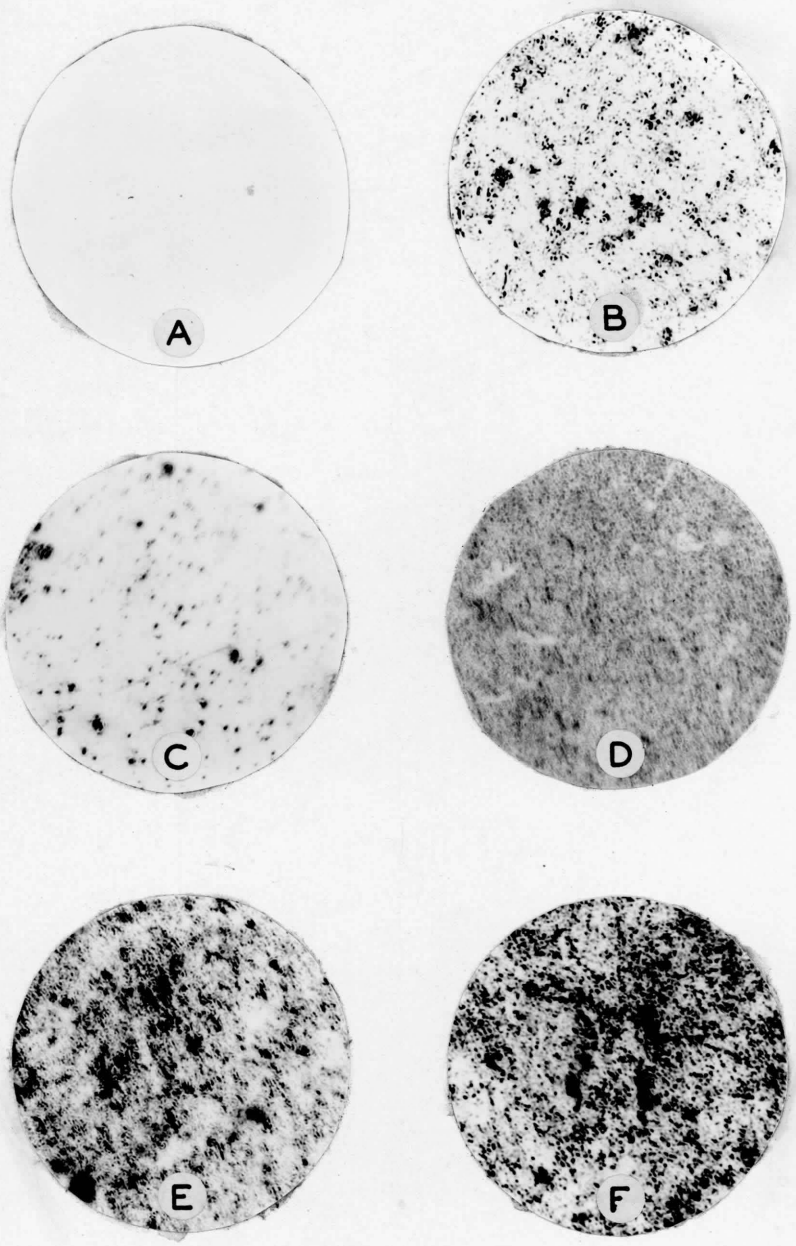
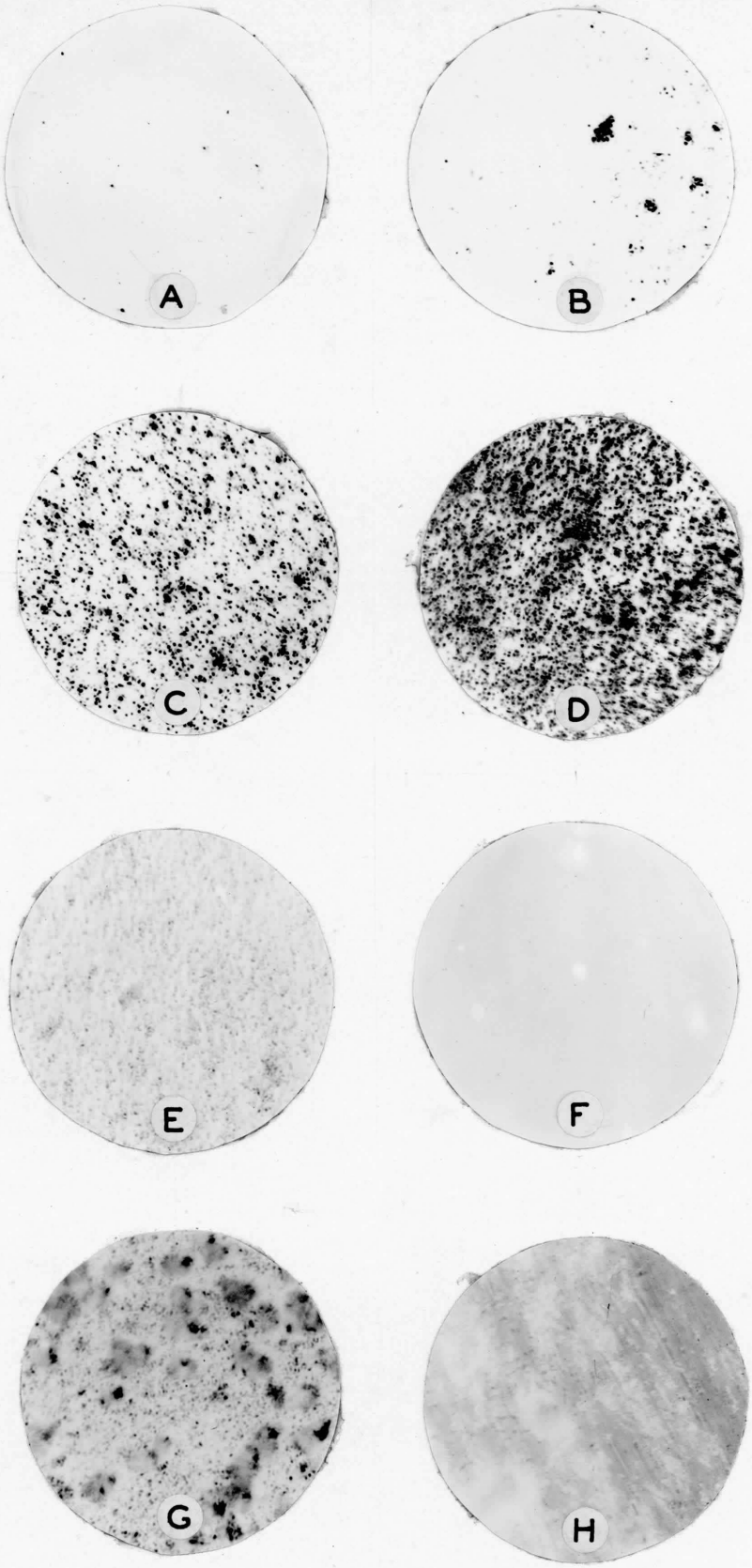


Figure 2 - Effect of corrosion of casing samples by immersion without applied potential. 300 X.

A. Polished specimen of steel pipe.
B. Corroded by immersion for 1.0 minute.
C. " " " " 2.5 "
D. " " " " 10 "
E. " " " " 30 "
F. " " " " 17 hours. Here the original polished surface has been entirely removed by corrosion.

Figure 3. Effect of cathodic protection of casing samples on reduction of corrosion. 300 X.

A. Polished specimen of steel pipe.
B. Corroded for 1 minute.
C. " " 2.5 minutes.
D. " " 10 "
E. " " 30 "
F. Same as E, except protective layer removed with lens paper.
G. Corroded for 17 hours.
H. Same as G, except protective layer removed with lens paper.


A
B
C
D
E
F
G
H

in the Tohill brine, B shows the surface after it had been immersed for 1 minute, C for 2.5 minutes, D. for 10 minutes, E for 30 minutes, and G for 17 hours. Photomicrographs F and H show specimens E and G, respectively, with the surface film removed by lens paper. While moist, the film is readily removed, but its removal becomes more difficult when dried. Although with the film removed the surfaces appear slightly stained, there is no visual evidence of corrosion.

The film appears to be composed of a partially reduced iron compound (probably iron hydroxide) and salts crystallized from the brine.

Anodic potential. - Figure 4 is a set of six photomicrographs which show various stages of corrosion of a polished surface of casing subjected to anodic current density of 1.2 ma. per sq. in. Photomicrograph A shows the polished surface before immersion in the Tohill brine, B shows the surface after it had been corroded for 1 minute, C. for 2.5 minutes, D for 10 minutes, E for 30 minutes, and F for 17 hours. A comparison of this figure with figure 2 shows that the rate of corrosion is accelerated by applied anodic potential.

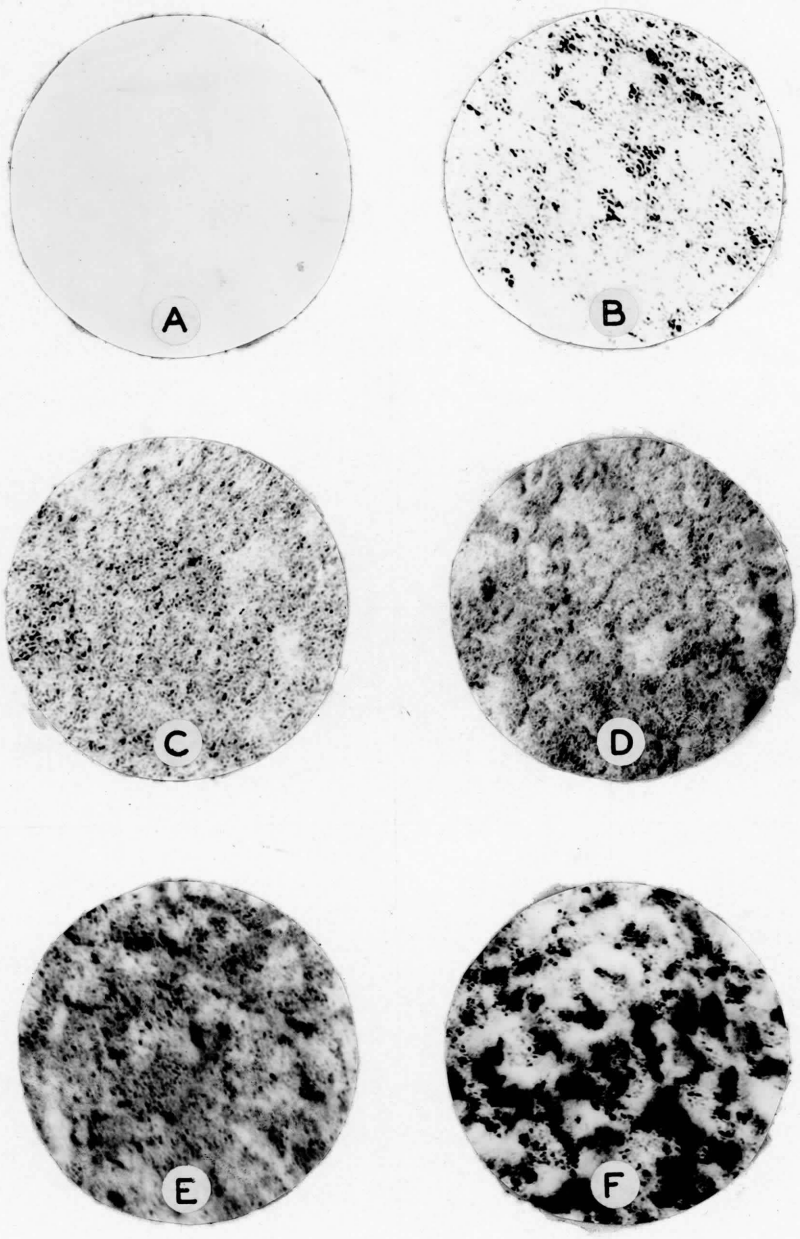


Figure 4. Effect of corrosion on an anodic casing sample. 300 X.

A. Polished specimen of steel pipe.
B. Corroded for 1 minute.
C. " " 2.5 minutes.
D. " " 10 "
E. " " 30 " Here the original polished surface has been entirely removed by corrosion.
F. Corroded for 17 hours.

In order to ascertain if the roughness of the area polished previous to corrosion is due to a film, an attempt was made to re-polish the area with lens paper. The failure to do so indicated that the roughness was due solely to the removal of metal.

Quantitative comparison of rates of corrosion as determined by changes in weight

The results of a series of tests, each lasting one month, are recorded in tables 2 to 7, inclusive. Table 2 shows the changes in weight of aamples of cathodic casing and anodic tubing continuously immersed with various current densities in Jones brine; whereas table 3 shows the resultant effect of reversing polarity of the casing and tubing. Table 4 shows the effect of intermittent immersion. Table 5 compares the corrosive effects of continuous immersion in the Tohill and Vinsel brines with that of the Jones brine. Table 6 shows the relative effect of intermittent immersion in these three brines. Table 7 compares the anodic rate of corrosion of cast iron and galvanized steel to that of drawn steel tubing.

Table 2

Changes in weight of samples of cathodic casing and anodic tubing continuously immersed with various current densities in Jones brine for a period of one month

Cathodes (casing)					Anodes (tubing)			
Current density (ma. per sq. in.)	Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)	Current density (ma. per sq. in.)	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
0.0	a	3664.6	3668.6	+0.11	0.0	822.0	822.8	+0.10
0.0	b	2935.0	2917.5	-0.60	0.0	846.6	846.0	-0.07
0.0	c	3658.0	3642.0	-0.44	0.0	763.3	765.8	+0.33
0.1	a	3640.0	3642.5	+0.07	0.3	773.2	770.6	-0.34
0.1	b	2879.5	2884.5	+0.17	0.3	761.7	759.8	-0.25
0.1	c	3748.5	3752.0	+0.09	0.3	786.4	783.8	-0.33
0.15	a	3599.7	3600.0	+0.01	0.45	818.4	815.8	-0.32
0.15	b	3644.0	3647.0	+0.08	0.45	800.1	799.2	-0.11
0.15	c	3772.0	3784.0	+0.32	0.45	767.9	768.7	+0.10
1.6		3624.9	3642.0	+0.47	4.8	776.9	779.0	+0.27
3.0		3629.4	3624.9	-0.12	9.0	814.3	776.9	-4.6

Table 3

Changes in weight of samples of cathodic tubing and anodic casing continuously immersed with various current densities in Jones brine for a period of 1 month

Cathodes (tubing)					Anodes (casing)			
Current density (ma. per sq. in.)	Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)	Current density (ma. per sq. in.)	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
0.9	a	818.8	818.4	-0.05	0.3	3618.0	3599.7	-0.51
0.9	b	800.6	800.1	-0.06	0.3	3656.0	3644.0	-0.33
0.9	c	766.9	767.9	-0.13	0.3	3788.0	3772.0	-0.42
9.0	a	771.9	773.2	+0.17	3.0	3668.0	3640.0	-0.76
9.0	b	761.1	761.7	+0.08	3.0	2908.0	2879.5	-0.98
9.9		785.1	786.4	+0.17	3.3	3782.0	3748.5	-0.89

Table 4

Changes in weight of samples of cathodic casing and anodic tubing intermittently immersed with various current densities in Jones brine for a period of one month

Cathodes (casing)				Anodes (tubing)			
Current density (ma. per sq. in.)	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)	Current density (ma. per sq. in.)	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
0.0	3658.0	3658.1	+0.003	0.0	850.7	850.7	0.0
1.6	2913.2	2922.5	+0.32	4.8	765.5	773.6	+1.1
3.0	2194.5	2913.2	-0.05	9.0	789.0	765.5	-1.7

Table 5

Changes in weight of samples of cathodic casing and anodic tubing continuously immersed in Jones, Tohill, and Vinsel brines with a current density of 3.0 ma. per sq. in. of casing surface which is 9.0 ma. per sq. in. of tubing surface, for a period of one month

Brine used	Cathodes (casing)			Anodes (tubing)		
	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
Jones	3629.4	3624.9	-0.12	814.3	776.9	-4.6
Tohill	3636.4	3609.0	-0.75	800.8	798.9	-0.24
Vinsel	2955.6	2942.0	-0.46	809.7	773.3	-0.79

Table 6

Changes in weight of samples of cathodic casing and anodic tubing intermittently immersed in Jones, Tohill, and Vinsel brines for a period of one month

Brine used	Cathodes (casing)				Anodes (tubing)			
	Current density (ma. per sq.in.)	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)	Current density (ma. per sq. in.)	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
Jones					0.0	850.7	850.7	0.0
Tohill					0.0	789.3	789.1	-0.03
Vinsel					0.0	805.3	805.5	+0.02
Jones	3.0	2914.5	2913.2	-0.05	9.0	789.0	765.5	-1.7
Tohill	3.0	3786.5	3783.5	-0.08	9.0	799.0	768.9	-3.8
Vinsel	3.0	3788.3	3786.1	-0.06	9.0	781.7	766.1	-2.0

Table 7

Changes in weight of samples of anodic drawn steel, cast iron, and galvanized steel tubing intermittently immersed in Jones brine for a period of one month

	Anodes (tubing)			
Tubing material	Current density (ma. per sq. in.)	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
Drawn steel	4.8	765.5	773.6	+1.1
Cast iron	4.8	1044.9	1043.5	-0.13
Galvanized steel	4.8	819.2	814.1	-0.61
Drawn steel	9.0	789.0	765.5	-1.7
Cast iron	9.0	1067.3	1044.9	-1.2
Galvanized steel	9.0	873.1	819.2	-6.1

Effect of current density on rate of corrosion

Continuous immersion. - Table 2 shows the changes in weight of samples of cathodic casing and anodic tubing continuously immersed in Jones brine with various current densities. The first three sets of samples were corroded without applied potential. The slight increase of weight of the tubing is doubtless due to the formation of adherent oxide which was difficult to remove before reweighing. The second three sets of samples were subjected to a current density of 0.1 ma. per sq. in. of casing surface which is equivalent to 0.3 ma. per sq. in. of tubing surface. The results show cathodic protection and a definite anodic corrosion. The third three sets of samples were subjected to a current density on casing and tubing surfaces of 0.15 and 0.45 ma. per sq. in., respectively. This slightly higher current density likewise provides cathodic protection at the expense of anodic corrosion. The fourth set of samples with current densities on casing and tubing of 1.6 and 4.8 ma. per sq.

in., respectively, shows cathodic protection and also a gain in weight of the anode, probably due to the formation of oxide. The fifth set of samples with current densities on casing and tubing of 3.0 and 9.0 ma. per. sq. in., respectively, shows a slight cathodic loss, probably due to spray, and a very large anodic loss.

Table 3 shows the effect of reversing the polarity of the casing and tubing, i.e., making the tubing samples cathodic and the casing samples anodic. The first three sets of samples with current densities of 0.9 and 0.3 ma. per sq. in. on tubing and casing, respectively, show a small cathodic loss and a much larger anodic loss. The second two sets of samples with current densities on tubing and casing of 9.0 and 3.0 ma. per sq. in,, respectively, show cathodic protection with attendant anodic corrosion. The third set of samples were subjected to current densities on tubing and casing of 9.9 and 3.3 ma. per sq. in., respectively. This higher current density provides cathodic protection and increases the amount of anodic corrosion.

Intermittent immersion. - Table 4 shows the changes in weight of samples of cathodic casing and anodic tubing intermittently immersed in Jones brine with various current densities. The first set of samples were corroded without applied potential. The fact that the samples show no weight loss may again be attributed to the difficulty of cleaning the oxide from the surfaces before reweighing. The second set of samples with current densities on casing and tubing of 1.6 and 4.8 ma. per sq. in., respectively, shows cathodic protection and a gain in weight of the anode due to formation of oxide film. The third set of samples with current densities on casing and tubing of 3.0 and 9.0 ma. per sq. in., respectively, shows a slight cathodic loss (due to spray), and a much larger anodic loss.

The results for both continuous and intermittent immersion indicate that protection is given the cathodic samples. It should be mentioned that with higher current densities there is a considerable evolution of gases from the brine with attendant splashing of the brine on the surface of the cathode above the solution level. Corrosion of this

unprotected part of the cathode surface accounts for the recorded loss of weight of the sample as a whole.

The rate of corrosion of an anodic sample is greater than that of a sample without applied potential, thereby showing that cathodic protection is afforded at the expense of anodic corrosion.

The divergence of results under duplicate conditions is attributed to irregularities of the surface condition of the samples.

Effect of various brines on rate of corrosion

Continuous immersion.- Table 5 shows the relative effects of Jones, Tohil and Vinsel brines on the rate of corrosion of continuously immersed samples of cathodic casing and anodic tubing subjected to current densities of 3.0 and 9.0 ma. per sq. in., respectively. The set of samples immersed in Jones brine, shows a slight cathodic loss and a large anodic loss. The set of samples immersed in Tohill brine, also shows a slight cathodic loss and anodic loss. The set of samples immersed in Vinsel brine, shows

a slight cathodic loss with a comparatively large anodic loss.

Intermittent immersion. - Table 6 shows the corresponding results for intermittent immersion in the three brines both without and with applied potential. Without applied potential only tubing samples were tested. Results for Jones brine show no change in weight, whereas those for Tohill and Vinsel brines show a slight loss and a slight gain, respectively. The irregular behavior of weight changes is due to surface conditions.

In the second series of tests, all samples were subjected to current densities on casing and tubing of 3.0 and 9.0 ma. per sq. in., respectively. The set immersed in Jones brine shows a small cathodic loss and an anodic loss thirty times as large. The set immersed in Tohill brine shows a greater cathodic loss than the Jones brine sample and an anodic loss almost fifty times that the the cathode. The set immersed in Vinsel brine shows cathode and anode losses intermediate between those found in Jones and Tohill brines. The results of tests on the weight changes of samples immersed in the three brines indicate that the Tohill brine is the most corrosive

with Vinsel brine intermediate, and Jones brine least corrosive.

Effect of anode metal on rate of corrosion

Table 7 shows the changes in weight of samples of anodic drawn steel, cast iron, and galvanized steel tubing intermittently immersed in Jones brine. These three different anodes were each tested at two different current densities, 4.8 and 9.0 ma. per sq. in,, respectively. At the lower current density there is an anodic gain for the drawn steel tubing, a small anodic loss for the cast iron tubing, and a large anodic loss for the galvanized tubing. At the higher current density, the anodic loss is practically identical for the drawn steel and the cast iron tubimgs, but very much greater for the galvanized steel tubing.

The results on weight changes of samples of drawn steel, cast iron, and galvanized steel anodic tubing samples intermittently immersed in Jones brine show that the rates of corrosion of the drawn steel and cast iron samples were about the same, whereas the galvanized steel corroded about five time as fast as the others.

This is to be expected, since zinc has a higher anodic solubility than iron. Visual inspection of the samples revealed the facts that the cast iron was more subject to pitting than the drawn steel, and that the zinc surface of the galwanized sample dissolved more rapidly in regions near breaks in the coating. This rapid removal of the zinc surface was due to local electrolytic currents between the anodic zinc surface and the exposed iron, which is cathodic to zinc. The above data indicate that drawn steel and cast iron tubing are equally subject to corrosion and that the galvanized coating is subject to rapid solution.

Minimum current density required for cathodic protection

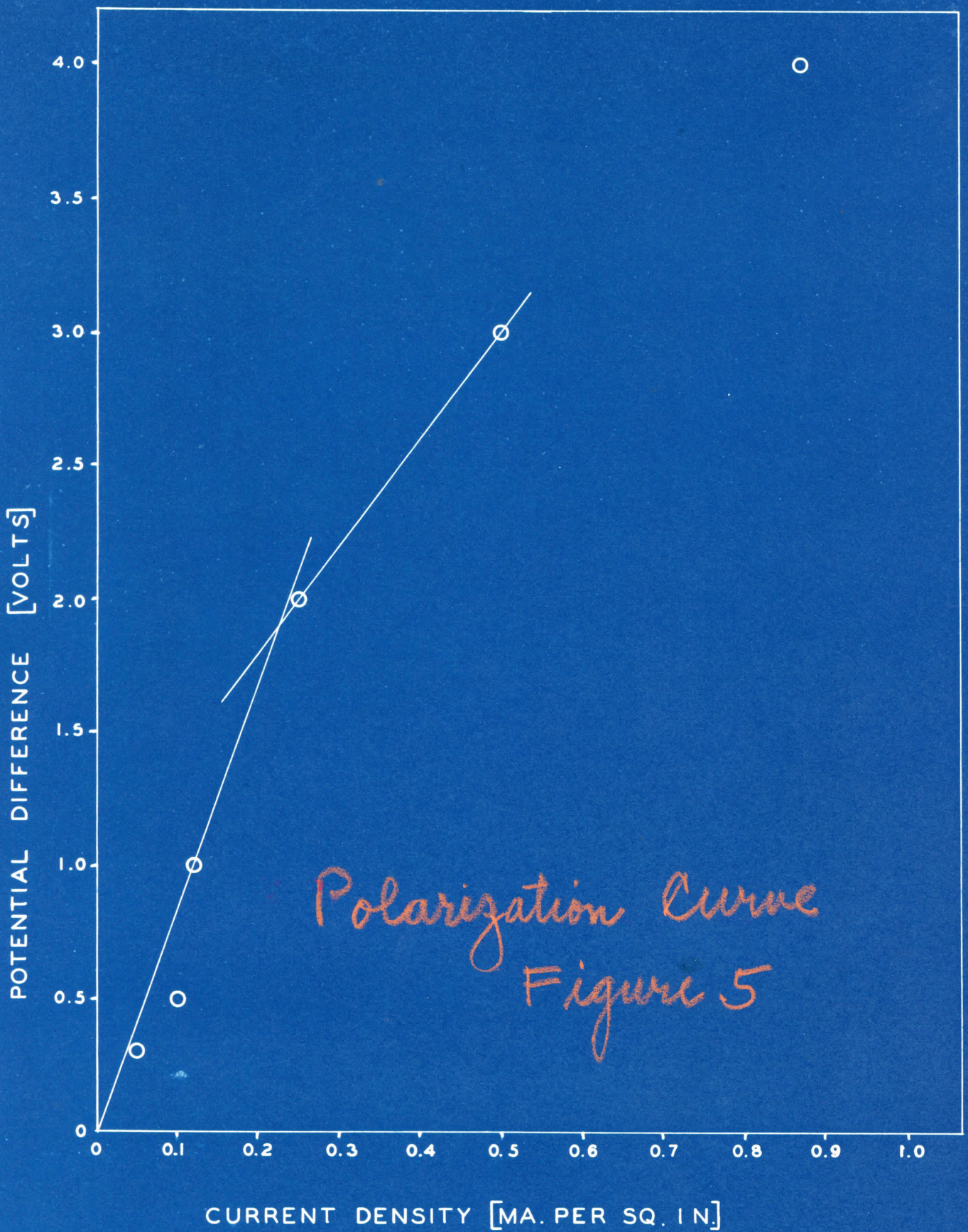
Theoretically cathode protection is due to the formation of a hydrogen film on the cathode which prevents the metal from going into solution in the brine. The maintenance of this protective hydrogen film requires a minimum applied potential equal to the polarization voltage of hydrogen, the experimental value of which

may be determined graphically from a diagram of current density and voltage. The value of the polarization voltage is determined by a break in the curve. And the corresponding minimum current density necessary to give cathodic protection against corrosion may be read directly from the graph.

In the determination of the polarization voltage, the Tohill brine was selected because it is the most corrosive of the three brines investigated.

Figure 5 (table 8) shows the resultant polarization curve. Straight lines are drawn through the points at zero and 1 volt and those at 2 and 3 volts. These lines intersect at a value of approximately 1.9 volts, this being the determined polarization voltage of hydrogen on an iron cathode in this brine. The current density corresponding to this voltage is 0.23 ma. per sq. in., this being the minimum value necessary to afford full cathodic protection.

It should be noted that other cathode metals and brines will have characteristic hydrogen polarization voltages, with different numerical values and therefore different minimum current densities necessary to give cathodic protection.



Polarization Curve
Figure 5

Table 8

Potential differences in volts between samples of drawn steel anodic tubing and cathodic casing immersed in Tohill brine, for various currents in amperes passing from tubing to casing. The currents are also expressed as current densities in milliamperes per square inch of casing surface

(Data for Fig.5)

Potential difference (volts)	Current (amperes)	Current density (ma. per sq.in.)
0.3	0.002	0.05
0.5	0.004	0.10
1.0	0.005	0.12
2.0	0.010	0.25
3.0	0.020	0.50
4.0	0.035	0.87

Cold rolled steel strip samples

Qualitative comparison of rates of corrosion as determined by photographs and photomicrographs

Corrosion tests on cold rolled steel strip samples, unless otherwise specified, were made with Tohill brine, selected because it was found to be the most corrosive brine investigated. The tests, unless otherwise stated, all lasted for a period of two weeks.

Figures 6, 7, and 8, are natural size photographs, each showing corroded anodic, neutral, and cathodic samples, A, B, and C. respectively.

Figure 6 shows samples corroded by continuous immersion with a current density of 0.22 ma. per sq. in. Figure 7 shows samples corroded by continuous immersion with a current density of 2.2 ma. per sq. in. Figure 8 shows samples corroded by intermittent immersion with a current density of 1.1 ma. per sq. in. The immersion line may be readily seen about half way up on all the samples.

Figure 9 is a photomicrograph of the smooth, cleaned surface of a steel strip sample before corrosion testing. The marks left by the rolls are quite sharp and distinct.

Figure 6. Steel strip samples, anodic (A), neutral (B), and cathodic (C) continuously immersed in Tohill brine for two weeks with a current density of 0.22 ma. per sq. in. Natural size.

Figure 7. Steel strip samples, anodic (A), neutral (B), and cathodic (C), continuously immersed in Tohill brine for two weeks with a current density of 2.2 ma. per sq. in. Natural size.

Figure 8. Steel strip samples, anodic (A), neutral (B), and cathodic (C) intermittently immersed in Tohill brine for two weeks with a current density of 1.1 ma. per sq. in. Natural size.

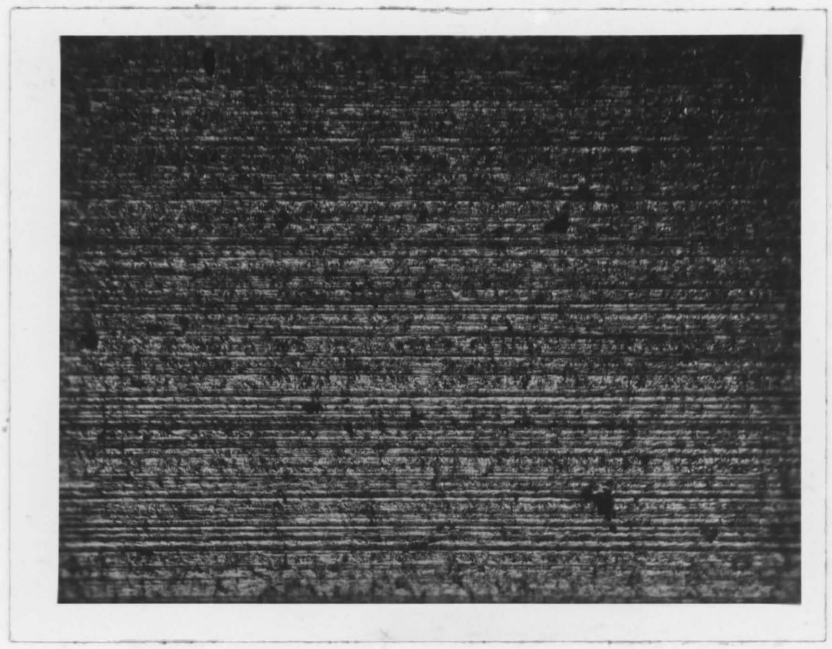


Figure 9. Surface of steel strip sample before corrosion testing. 40 X.

Figure 10 is a set of five photomicrographs showing the effect of various current densities on the rate of corrosion of samples which have been continuously immersed.

Figure 11 is a set of seven photomicrographs showing the effect of various current densities on the rate of corrosion of samples which have been intermittently immersed.

Figure 12 is a photomicrograph of the pits occurring at the immersion level on an anodic sample which has been continuously immersed with 2.2 ma. per sq. in. current density.

Figure 13 is a natural size photograph of an anodic (A) and cathodic (B) sample which have been continuously immersed in a normal salt solution (58.5 grams of sodium chloride per liter), for three weeks with 0.22 ma. per sq. in. current density. The surfaces of these two samples were cross hatched with lines of paraffin wax before immersion so that the uniformity of corrosion over their surfaces could be investigated.

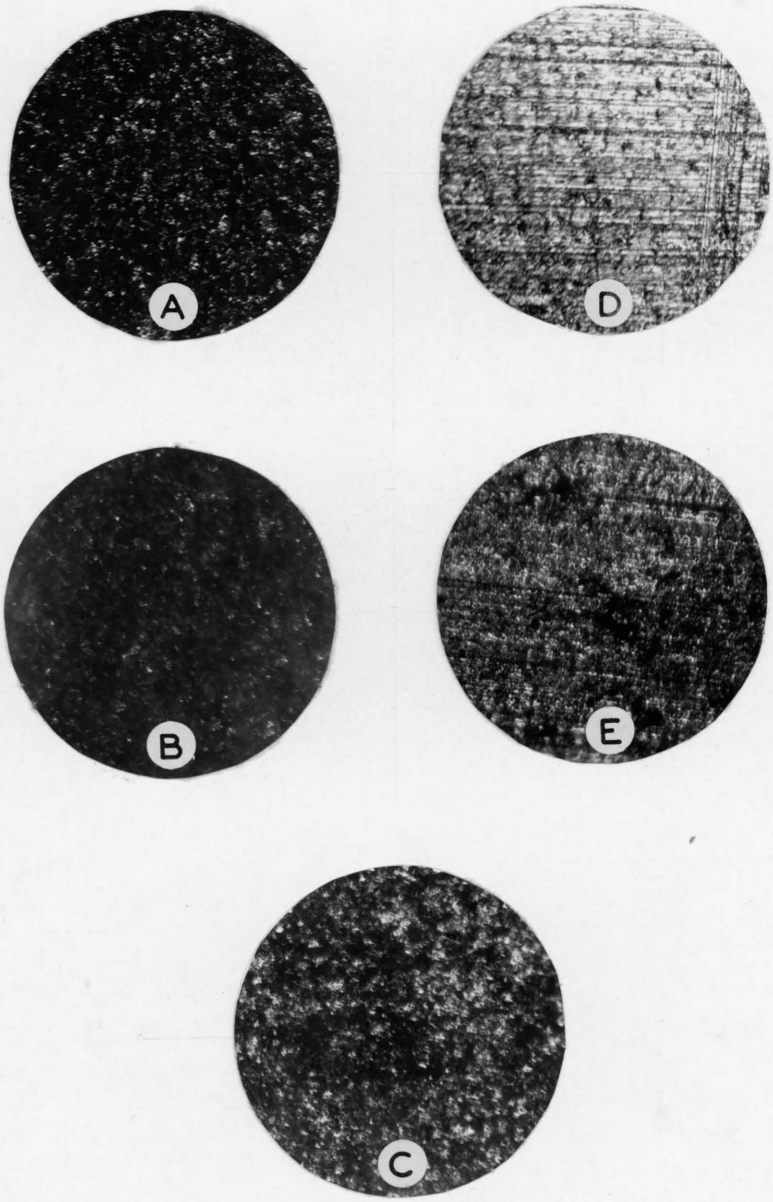
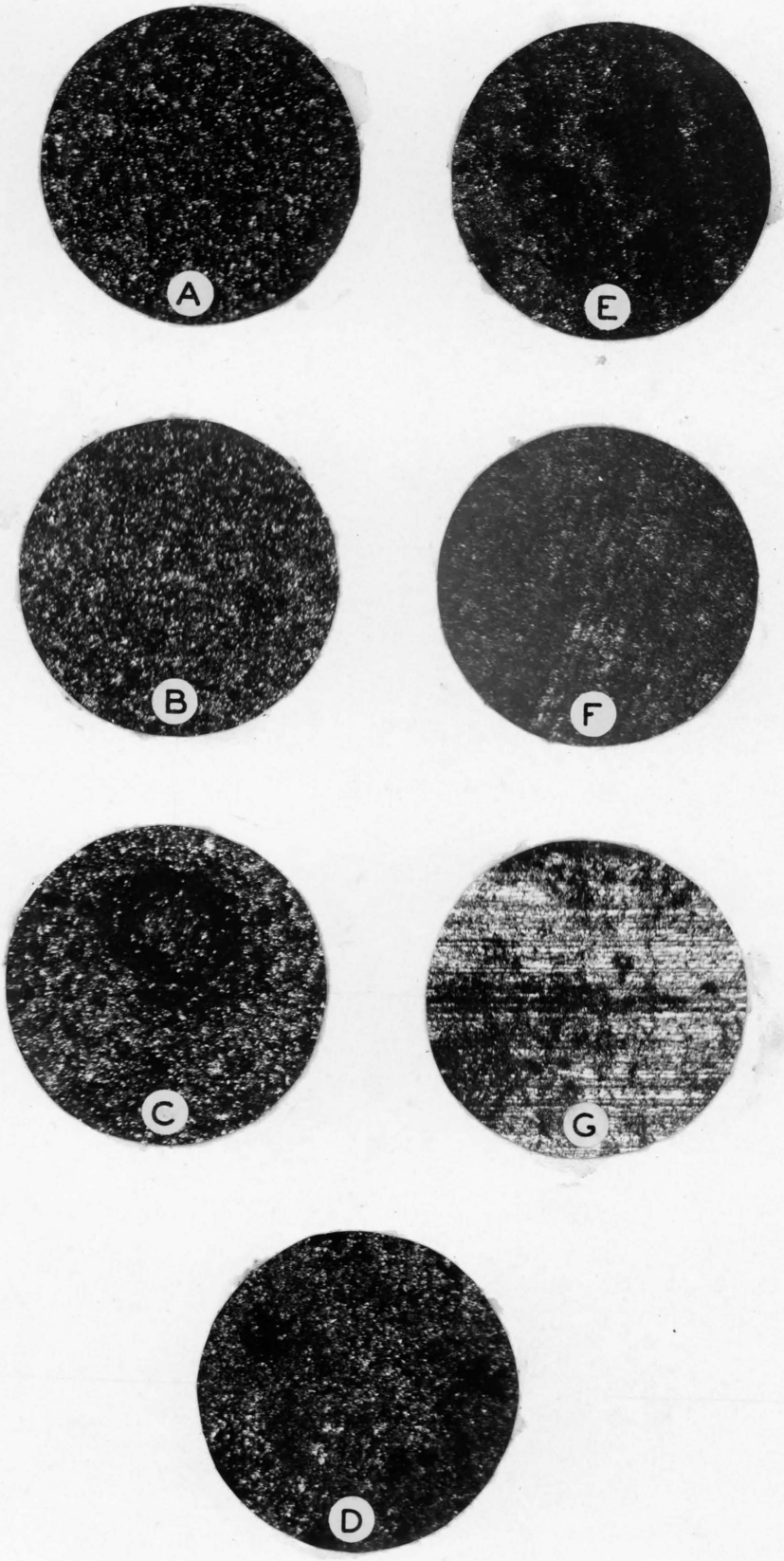


Figure 10. Effect of various current densities on rate of corrosion of steel strip samples continuously immersed in Tohill brine for two weeks. 40 X.

A. Anode 2.0 ma.
B. Anode 20.0 ma
C. Unprotected
D. Cathode 2.0 ma.
E. Cathode 20.0 ma.

Figure 11. Effect of various current densities on rate of corrosion of steel strip samples intermittently immersed in Tohill brine for two weeks. 40 X.

A. Anode; 0.5 m.a.
B. Anode; 1.0 m.a.
C. Anode; 10.0 m.a.
D. Unprotected.
E. Cathode; 0.5 m.a.
F. Cathode; 1.0 m.a.
G. Cathode; 10.0 m.a.


A
E
B
F
C
G
D

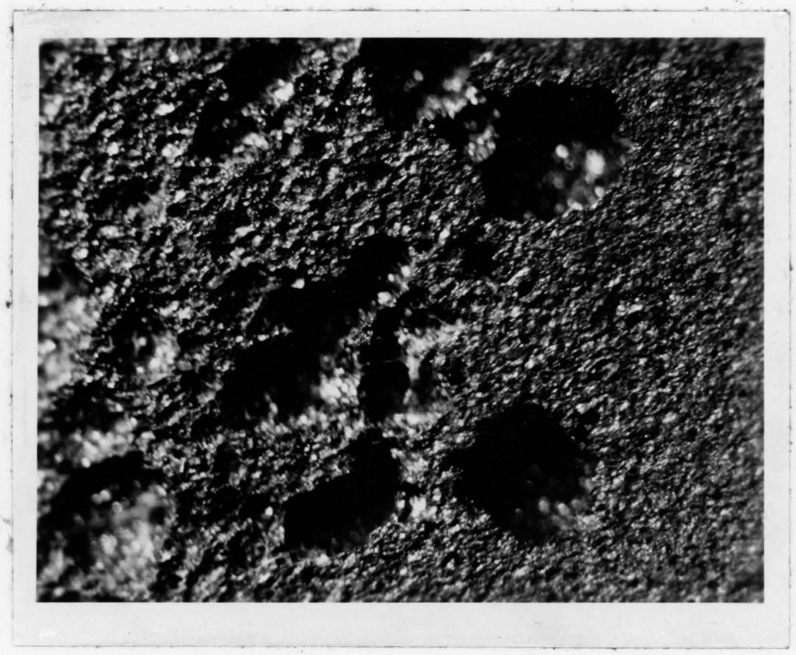


Figure 12. Pits at solution level on anodic steel strip sample continuously immersed with a current density of 2.2 ma. per sq. in. in Tohill brine for two weeks. 40 X.

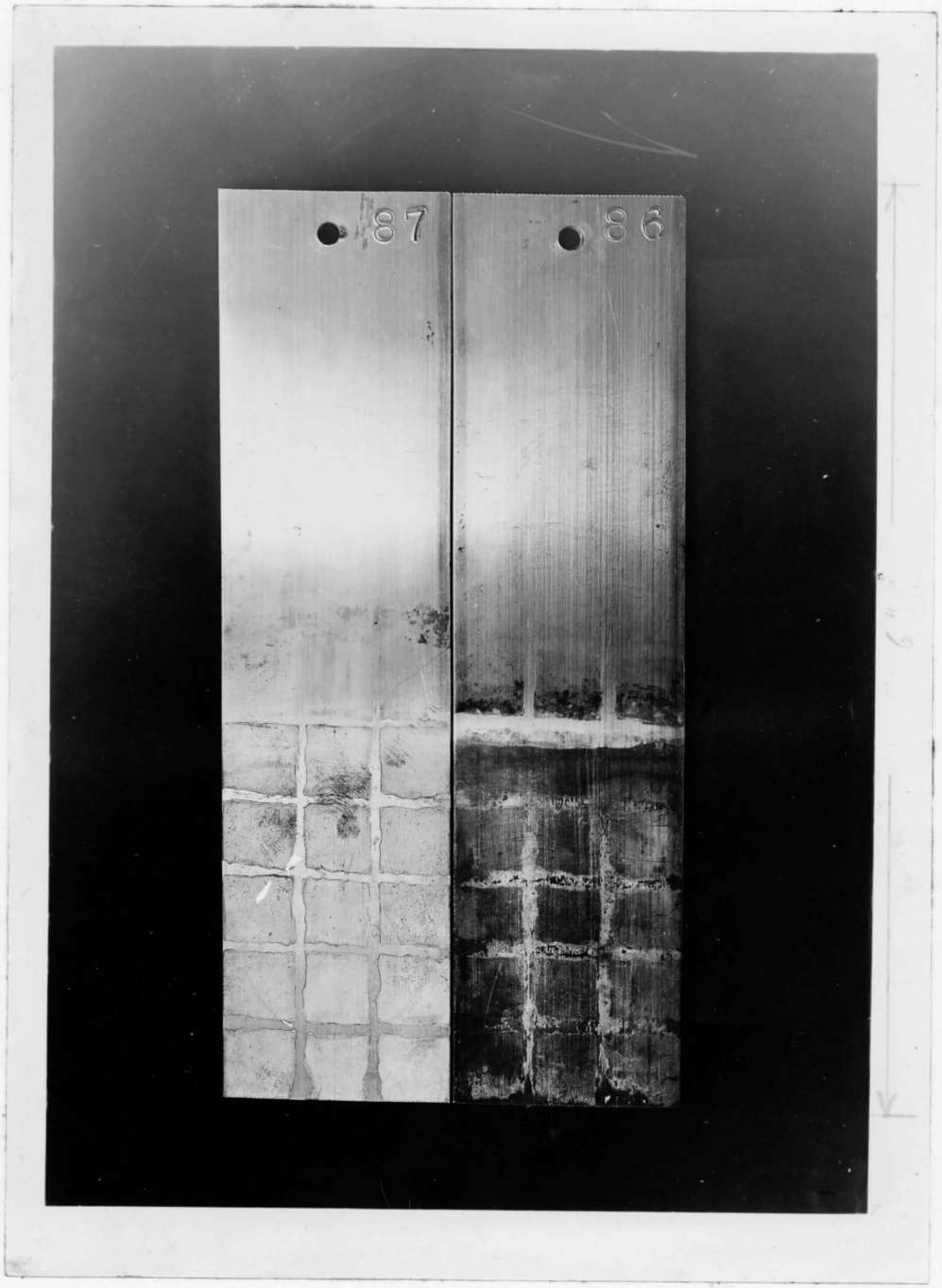


Figure 13. Degree of uniformity of corrosion of anodic (A) and cathodic (B) steel strip samples continuously immersed in a normal salt solution for three weeks with a current density of 0.22 ma. per sq. in. 40 X.

Figure 14 is a set of two photomicrographs showing the effect of the presence of oxygen on the rate of corrosion of samples continuously immersed without applied potential in the Tohill brine.

Without applied potential

A comparison of the appearance of the sample shown in figure 8B for intermittent immersion with those in figures 6B and 7B for continuous immersion shows that the rate of corrosion is distinctly greater for intermittent immersion. This same conclusion may be drawn from the comparison of the appearance of the photomicrographs shown in figures 11D and 10 C for intermittent and continuous immersion, respectively.

With applied potential

Cathodic potential. - A comparison of the appearance of the samples shown in figures 6C and 7C, cathodically protected during continuous immersion with that shown in figure 8C for intermittent immersion shows that a much greater degree of cathodic protection

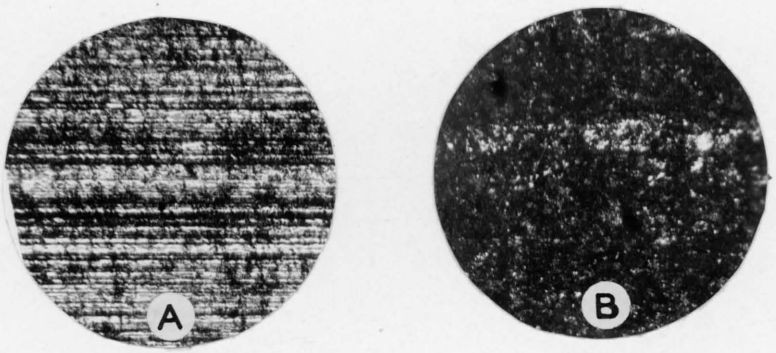


Figure 14. Effect of oxygen (air) on rate of corrosion by continuous immersion in Tohill brine without applied potential for two weeks. Specimen (A) protected from air, (B) open to air. 40 X.

is afforded under conditions of continuous immersion. But a comparison of these figures with figures 6B, 7B, and 8B, representing conditions without applied potential, shows conclusively that cathodic potential does protect against corrosion for both continuous and intermittent immersion.

Furthermore, a comparison of the appearance of samples shown in figures 6C and 7C, representing cathodic protection for continuous immersion at current densities of 0.22 and 2.2 ma. per sq. in., respectively, shows no evidence of increased corrosion protection at the higher current density.

Further definite evidence of cathodic protection is afforded by the comparison of photomicrographs of cathodically protected samples shown in figure 10D and 10E with a corresponding sample prior to immersion shown in figure 9.

Figure 11E, F and G shows the comparative degree of corrosion of cathodic samples intermittently immersed with current densities of 0.06, 0.11 and 1.1 ma. per sq. in., respectively. Comparison with the uncorroded sample shown in figure 9, indicates that

although a slight degree of corrosion is visible in the cathodically protected samples, nevertheless a current density of 1.1 ma. per sq. in. results in excellent corrosion protection even under the unfavorable condition of intermittent immersion.

Anodic potential. - For continuous immersion a comparison of figure 6A with 7A, anodically corroded at current densities 0.22 and 2.2 ma. per sq. in., respectively, shows that rate of anodic corrosion increases with the increase of current density.

Also a comparison of these figures for continuous immersion with figure 8A for intermittent anodic immersion at a current density of 1.1 ma. per sq. in., indicates that about the same degree of anodic corrosion at a given current density results from either continuous or intermittent immersion.

A comparison of these three anodic samples with the corresponding samples (Figs. 6B, 7B and 8B) corroded without applied potential indicates that the rate of anodic corrosion is much greater than that of neutral corrosion. This further proves that cathodic protection is afforded at the expense of anodic corrosion.

The extreme degree of anodic corrosion is also indicated in the photomicrographs shown in figure 10A and B.

Figure 11A, B and C show photomicrographs of anodic samples intermittently immersed at various current densities. Again there is evidence of increased rate of anodic corrosion with increase of current density.

As mentioned previously in the instance of pipe samples, increased pitting at the brine level results from increased current density. This condition is illustrated by figure 12 which is a photomicrograph of the area at the brine level of the sample previously shown in figure 11C which was anodically corroded at the highest current density used. The excessive pitting, due to splashing, is quite evident. This accounts for the cathodic weight losses previously recorded for pipe samples corroded at high current densities. Due to the proximity of cathode to anode in these tests, the liberation of gases caused the splashing of brine on the surfaces of both electrodes.

Uniformity of corrosion. - In order to test the uniformity of corrosion over the near surfaces of the two parallel samples, portions of the surfaces were protected from corrosion by cross-hatching with wax. Figure 13 is a photograph of the anodic (specimen A) and cathodic (B) samples subjected to three weeks corrosion in a normal salt solution at a current density of 0.22 ma. per sq. in., the wax being previously removed. A close inspection of the anodic sample reveals very uniform corrosion except at the edges where the corrosion is more intense. The surface of the cathodic sample is quite uniform, little or no corrosion having taken place.

Effect of oxygen

In order to determine the effect of oxygen on the rate of corrosion, two strip samples were corroded without applied potential in two beakers of brine under identical conditions except that air was expelled and excluded from one brine sample and not from the other. The samples of brine were boiled to expel air and other

dissolved gases and the surface of one was immediately sealed over with wax to prevent admission of air. The other brine was agitated when cool to entrap air and thereafter left exposed, distilled water being added as required to replace evaporation losses. Figure 14A and B show photomicrographs of the samples corroded in brines free from oxygen, and with oxygen, respectively. The presence of oxygen greatly accelerates the rate of corrosion.

Quantitative comparison of rates of corrosion as determined by changes in weight

All the corrosion tests on the changes in weight of steel strip samples lasted two weeks and were made with Tohill brine.

Table 9 shows the changes in weight of samples corroded by continuous and intermittent immersion without applied potential.

Tables 10 and 11 show the changes in weight of cathodic and anodic samples continuously immersed with current densities of 0.22 and 2.2 ma. per sq. in., respectively.

Table 12 shows the changes in weight of cathodic and anodic samples intermittently immersed with a current density of 1.1 ma. per sq. in.

Table 9

Changes in weight of samples of cold rolled steel strip corroded by continuous and intermittent immersion in Tohill brine for a period of two weeks without applied potential

Continuous immersion				Intermittent immersion			
Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)	Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
a	71.92	71.79	-0.19	a	71.36	71.145	-0.30
b	71.21	71.09	0.17	b	71.95	71.735	0.30
c	72.00	71.875	0.17	c	71.24	71.005	0.33
d	71.38	71.24	0.20	d	71.30	71.06	0.33
e	71.225	71.095	0.18	e	71.59	71.365	0.31
f	71.28	71.16	0.17	f	71.90	71.685	0.30
g	71.35	71.225	0.17	g	71.145	70.905	0.34
h	71.40	71.265	0.19	h	71.75	71.52	0.32
Average change in weight			-0.18	Average change in weight			-0.32

Table 10

Changes in weight of cathodic and anodic samples of cold rolled steel strip continuously immersed with a current density of 0.22 ma. per sq. in. in Tohill brine for a period of two weeks

Cathodes				Anodes			
Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)	Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
a*	72.07			a	71.93	71.13	-1.1
b*	71.24			b	71.36	70.58	1.0
c	71.42	71.415	-0.007	c	72.19	71.40	1.0
d	71.21	71.21	0.0	d	71.28	70.50	1.0
e	71.69	71.69	0.0	e	71.40	70.615	1.0
f	71.27	71.27	0.0	f	71.55	70.755	1.0
g	71.98	71.985	+0.007	g	71.52	70.75	1.0
h	71.39	71.395	+0.007	h	71.12	70.345	1.0
i	71.68	71.675	-0.007	i	72.21	71.44	1.0
Average change in weight			0.0	Average change in weight			-1.0

* Samples spoiled by attempting to clean them electrolytically

Table 11

Changes in weight of cathodic and anodic samples of cold rolled steel strip continuously immersed with a current density of 2.2 ma. per sq. in. in Tohill brine for a period of two weeks

Cathodes				Anodes			
Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)	Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
a	71.18	71.145	-0.05	a	71.36	64.765	-9.3
b	71.79	71.780	0.01	b	71.92	65.205	9.4
c	72.03	71.980	0.07	c	71.955	65.450	9.0
d	71.50	71.495	0.007	d	71.42	64.92	9.1
e	71.325	71.320	0.007	e	71.275	64.815	9.1
f	71.40	71.390	0.01	f	71.77	65.31	9.0
g	71.94	71.930	0.01	g	71.86	65.36	9.0
h	71.955	71.955	0.0	h	71.97	65.47	9.0
i	72.10	72.060	0.05	i	71.78	65.29	9.0
Average change in weight			-0.02	Average change in weight			-9.1

Table 12

Changes in weight of cathodic and anodic samples of cold rolled steel strip intermittently immersed with a current density of 1.1 ma. per sq. in. in Tohill brine for a period of two weeks

Cathodes				Anodes			
Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)	Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
a	71.405	71.370	-0.05	a	71.345	67.97	-5.0
b	71.43	71.385	0.06	b	71.59	68.22	5.0
c	71.22	71.175	0.06	c	71.875	68.485	5.0
d	71.25	71.190	0.08	d	71.71	68.305	5.0
e	71.98	71.935	0.06	e	71.03	67.635	5.0
f	71.94	71.890	0.07	f	72.12	68.470	5.0
g	72.26	72.220	0.06	g	71.11	67.720	5.0
h	71.34	71.305	0.05	h	71.95	68.575	4.9
i	71.77	71.730	0.06	i	71.22	67.820	5.0
Average change in weight			-0.06	Average change in weight			-5.0

Table 13 shows the effect of various current densities on the rate of cathodic and anodic corrosion for intermittent immersion.

Without applied potential

Table 9 shows the effects of continuous and intermittent immersion without applied potential on the rate of corrosion. The average weight loss for samples corroded by continuous immersion is 0.18 per cent; by intermittent immersion, 0.32 per cent. This indicates that the rate of corrosion for intermittent immersion is about 78 per cent greater than that for continuous immersion.

With applied potential

Cathodic potential. - Table 10 shows the changes in weight of samples continuously immersed with a current density of 0.22 ma. per sq. in. The first two cathodic samples listed were spoiled by attempting to clean them electrolytically. The remainder of the cathodic samples show a remarkable uniformity in weight changes, the values of which are negligible.

Table 11 shows the corresponding effect of a current density

Table 13

Changes in weight of cathodic and anodic samples of cold rolled steel strip intermittently immersed with various current densities in Tohill brine for a period of two weeks

	Cathodes				Anodes			
Current density (ma. per sq. in.)	Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)	Sample	Initial weight (gm.)	Final weight (gm.)	Change in weight (per cent)
0.055	a	72.600	72.465	-0.2	a	72.440	71.930	-0.7
0.055	b	72.410	73.310	-0.1	b	72.055	71.575	-0.7
0.11	a	71.085	71.035	-0.05	a	71.255	70.580	-0.9
0.11	b	71.240	71.190	-0.05	b	71.280	70.640	-0.9
0.22	a	72.205	72.215	+0.01	a	72.045	71.265	-1.1
0.22	b	71.680	71.660	-0.03	b	71.855	71.095	-1.1

of 2.2 ma. per sq. in., other conditions being the same as in the above test. In this instance, the cathodes show a small average weight loss due to pitting caused by excessive gassing with resultant splashing of the brine.

Table 12 shows the changes in weight of samples intermittently immersed with a current density of 1.1 ma. per sq. in. The cahtodic samples show a definite weight loss due to corrosion during the periods that the samples are removed from the brine.

Table 13 shows the changes in weight of samples intermittently immersed with various current densities up to a value of 0.22 ma. per sq. in. With increasing current densities the cathodes show an increasing degree of cathodic protection. Excellent cathodic protection, even for intermittent immersion conditions was afforded by the highest current density investigated.

Anodic potential. - Referring again to tables 9 and 10, it is seen that the anodic rate of corrosion at a current density of 0.22 ma. per sq. in. under conditions of continuous immersion is 5.5 times as great as that for a sample corroded without applied potential.

This again indicates that cathodic protection is afforded at the expense of increased anodic corrosion.

A comparison of tables 10 and 11 indicates that, under conditions of continuous immersion, a ten-fold increase in current density results in an approximate ten-fold increase in the rate of anodic corrosion.

Table 12 shows a 5 per cent anodic loss for samples intermittently immersed at a current density of 1.1 ma. per sq. in. An interpolation of the data shown in table 11 for continuous immersion shows a corresponding average anodic loss of 4.55 per cent for the same current density, thereby indicating about the same rate of anodic corrosion for intermittent and continous immersion.

Table 13 shows that for intermittent immersion the anodic rate of corrosion increases with current density. By extrapolation, a current density of 1.1 ma. per sq. in. would result in an anodic corrosion of 5.5 per cent, which is approximately the value noted above.

Minimum current density required for cathodic protection

Table 10 shows that complete cathodic protection is realized with a current density of 0.22 ma. per sq. in. for continuous immersion. Referring to figure 5, it was shown by the break in the polarization curve that the theoretical minimum current density for cathodic protection is 0.23 ma. per sq. in. This shows a striking agreement between the theoretical and determined values.

Effect of oxygen

A strip sample immersed in brine which was open to the air showed a loss in weight after two weeks of 0.37 per cent. A similar sample, immersed in brine from which gases had been expelled by boiling and had then been sealed over with a layer of wax, showed a loss in weight of 0.012 per cent for a similar period. The presence of air accelerated corrosion 31 fold.

Increase of life due to cathodic protection

At the preferred current density (0.22 ma. per sq. in.) to give corrosion protection under conditions of continuous immersion, table 10 indicates no lessening of the life of the cathodic sample due to corrosion. But a comparison of this table with table 9 shows that this complete cathode corrosion protection is afforded by a six-fold increase in rate of corrosion of a similar sample which serves as an anode.

For the same conditions with intermittent immersion, table 13 shows that cathodic protection results in a 32 fold increase of life at the expense of 3.4 fold increase in rate of anodic corrosion. As would be expected, continuous immersion provides better cathodic protection than intermittent immersion because in the latter, the cathodic sample is not afforded corrosion protection during the periods it is removed from the brine.

Feasibility of cathodic corrosion protection in the field

In a discussion of the applicability of cathodic corrosion protection for oil well casing, consideration may be given to both the use of applied potential and metals of different contact potential.

Protection by applied potential. - In field practice of cathodic corrosion protection by externally applied voltage, either the casing may be protected cathodically at the expense of the anodic tubing or cathodic protection may be afforded to both the casing and the tubing by the insertion of an intermediate anodic pipe.

As pointed out previously, both theoretical calculation and experimental results indicate that it requires a current density of about 0.23 ma. per sq. in. to afford complete cathodic corrosion protection. This is equivalent to 0.033 amp. per sq. ft. As stated previously (p.), normally about 200 feet of casing and tubing are subjected to intermittent immersion in the brine. For a six-inch casing this distance corresponds to about 300 sq. ft. inside surface area. This would require a total current of about 10 amps.

Standard size 2-inch tubing is 2 3/8 inches outside diameter, or the above distance corresponds to about 120 sq. ft. outside tubing area which would require a total current of about 4 amps. Therefore if both tubing and casing are protected by the use of a third electrode, the current requirement for a typical Illinois well would be about 14 amps.

Referring again to figure 5, it is seen that about 1.9 volts is required to furnish this current density. Including the drop of voltage in the electrical circuit, three volts would be more than sufficient. This may be secured by a 2-cell storage battery. A heavy duty battery would carry such a load for reasonable periods and may be recharged as required.

Although cathodic protection against corrosion by applied potential will greatly increase the life of oil well casing and tubing, only actual field practice can determine if the protection compensates for the cost of installation and maintenance.

Protection by contact potential. - Also in field practice, cathodic corrosion protection may be secured by the use of a metal electropositive to both the casing and tubing situated between them. A good material would be a solid zinc tubing, although probably prohibitive in cost. A reasonably satisfactory material is rusty iron pipe.

Independent of this investigation, Mr. M. J.Kinefake[1/] of the Tide Water Oil Company, used a modified form of this latter method. He made a test on a well in which the tubing corroded rapidly. Five badly corroded bottom lengths of wrought iron tubing were replaced with galvanized tubing. After six months service the galvanized tubing was examined, the two bottom lengths being found to be seriously corroded. These two lengths were replaced with new galvanized tubing. Then around each of the five bottom lengths of the galvanized tubing there was placed a length of 3-inch rusty iron pipe. The ends of these pipes were drawn in to make a snug fit, and their weight rested on

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1/ Private communication.

the galvanized tubing collars. This method has afforded corrosion protection for six years as contrasted to a previous life of probably less than a year. But Mr. Kenefake adds that this method did not afford the same degree of corrosion protection when used on certain other wells.

The positions of different metals in the electromotive series indicate that although a rusty iron pipe is anodic to a steel pipe before rusting, yet it is not anodic to the zinc coating on a galvanized iron pipe. This indicates a greater probability of success with the rusty iron pipe method of corrosion protection when used with a new steel tubing instead of galvanized steel tubing.

This latter method appears to hold greater commercial promise than the applied potential method of corrosion protection because it is less expensive in both installation and maintenance. Discarded piping may be used for the auxiliary electrode and no maintenance is required since externally applied current is not used.

The Survey recommends that the rusty iron pipe method of corrosion protection be fully investigated under various field conditions.

Aitchison, Leslie, - Experiments on the influence of composition upon the corrosion of steel. Trans. Faraday Soc. 11, 212-34 (1915).

Specimens of steel were allowed to corrode in brine, sulphuric acid solutions, and tap water. Resistance to corrosion depends equally on the solution and the composition of the metal.

Aitchison, Leslie, - Theory of the corrosion of steel. J. Iron and Steel Ind., 93, pt. 1, 77-101 (1916).

A theoretical discussion of corrosion.

Aston, James, and Burgess, C. F., - The rate of rusting of iron and steel. Trans. Am. Electrochem. Soc. 22, 219-40 (1912).

Rate of corrosion depends on structure and composition of metal and the conditions of exposure.

Aupperle, J. A., and Strickland, D. M., - Observations on the corrosion of iron and steel. Trans. Am. Electrochem. Soc. 39, 123-140 (1921).

Tests on various types of iron. In all cases pure iron made in open-hearth furnaces showed least corrosion.

Bancroft, W. D., - Corrosion in aqueous solutions. Ind. & Eng. Chem. 17, 336-8 (1925).

Theoretical discussion of corrosion.

Bancroft, W. D., - The electrolytic theory of corrosion. J. Phys. Chem., 28, 785-871, 1924.

Review of articles published on corrosion from 1903 to 1924.

Bancroft, W. D., - First report of the committee on contact catalysis. Ind. Eng. Chem. 14, 545 (1922).

The role played by the surface film in corrosion is emphasized.

Beeny, H., - Electrochemical method for estimating the corrosion of iron and steel. Am. Electrochem. Soc. Trans. 48, 103-117 (1925).

Use of salt solution in accelerated corrosion testing.

Bengough, G. D., and Stuart, J. M., - Nature of corrosive action, and function of colloids in corrosion. J. Inst. Metals, 28, 31-114 (1922).

Suggests corrosion by oxygen alone.

Blum, W., and Rawdon, H. S., - Principles of electrolytic studies on corrosion. Am. Electrochem. Soc. Trans. 52, 403-433 (1927).

Discuss - with experimental data - effect of current, potential, anode material, electrolyte, physical properties of anode material, polarization, and film on electrolytic corrosion.

Brown, Harold P., - Method of permanently protecting underground pipes from electrolytic corrosion. Street Ry. Rev. 5, 157 (1895).

Uses current with pipe at least one volt negative to rails.

Buck, D. M., - Observations on the mechanism of the increased corrosion resistance of steel and iron due to small copper content. Trans. Am. Electrochem. Soc. 39, 100-22 (1921).

0.2% of copper increases corrosion resistance. May be due to formation of solid solution formation of a film of copper on exposed surface, or to less liability for other elements present to segregate in spaces between grains of iron.

Burgess, C. F., - The corrosion of iron from the electrochemical standpoint. Trans. Am. Electrochemical Society 13, 17-48 (1908).

Discusses effect of strain upon corrosion - also effect of local temperature variations. Both cause local anodic areas.

Burgess, C. F., and Aston, James, - Influence of various elements on the corrodibility of iron. Trans. Am. Electrochem. Soc. 22, 241-58 (1912).

Acid corrosion and atmospheric corrosion only considered. External conditions must be considered, as well as composition of metal.

Byers, H. G., - Anodic relations of passive iron with notes on polarization as influenced by gas pressure. J. Am. Chem. Soc. 38, 362-74 (1916).

Anodic influence on the passivity of iron.

Carrick, O. W., - Prevention of sub-aqueous corrosion by electro-chemical polarization process. Am. Water Works Assn. J. 19, 704-13 (1928).

Locomotive boilers protected by current, using removable anodes, 2 mil-amp per square foot of surface, arsenic salts added occasionally to give an arsenic plating for further protection.

Chittum, J. F., - Electrochemical behavior of metals. J. Phys. Chem. 34, 2267-85 (1930).

Passivity intimately connected with corrosion resistance. Oxidizing conditions produce passivity.

Clement, J. E., and Walker, L. V., - An electrolytic method of preventing corrosion of iron and steel. U. S. Bur. Mines Tech. Paper No. 15, 17 pp. (1913).

Experimental determination of the magnitude of cathodic current density necessary to prevent corrosion.

Cranfield, W., - Iron: its oxidation, corrosion, protection. J. Gas Lighting 106, 443 (1909).

Discusses theory, corrosive agents and preservative coatings.

Cumberland, E., - Demonstration of the Cumberland electrolytic process for preventing corrosion of all metals immersed in liquids. Trans. Faraday Soc. 11, 277-281 (1915).

Uses zinc anodes electrically connected to boiler wall.

Cumberland, E., - Cumberland electrolytic system for the prevention of scale and corrosion. Electrician 81, 419 (1918).

Process consists of introducing steady flow of current at low voltage by means of suitably insulated anodes of cast iron.

Davis, R. O. E., - Corrosion of iron. Chem. Eng. 5, 174-5 (1907).

Claims that water and oxygen are the only essentials for corrosion.

Davy, Humphrey, - On the corrosion of copper sheathing by sea-water and methods of preventing this effect. Trans. Royal Society 114, 151 (1823-5).

Use of "protectors" of a metal more electropositive than copper to secure a differential corrosion due to galvanic battery effect.

Desch, Cecil H., - The micro-chemistry of corrosion. Trans. Am. Electrochem. Soc. 46, 241-246 (1924).

Colloids not necessary to corrosion. The slightest touch or stain or strain destroys the homogeneity of the specimen. Accepts electrochemical view.

Devine, J. M., Wilhelm, C. F., and Schmidt, Ludwig, - Oxygen effect on H_2S gas corrosion. Oil and Gas J. 30, #47, pp. 16+ (1932).

Laboratory experiments show corrosive factors to be composition, temperature, pressure of the gas, and its rate of flow, and time of exposure. It was found that the presence of oxygen is necessary for corrosion to take place.

Evans, U. R., - The mechanism of corrosion. J. Chem. Soc. p. 111-29 (1929).

Corrosion commences at weak points, especially along edges and corners. Type of corrosion and rate depend upon material and solution, because of the differences in the value of the unpolarized voltage with different solutions and metallic electrodes.

Evans, U. R., - The newer electrochemical view of the corrosion of metals. J. Soc. Chem. Ind. 43, 222-3, (1924).

A small cavity will become anodic due to its unaerated condition. Corrosion will occur faster here, and pitting takes place.

Evans, U. R., - Passivity of metals; the influence of acids in passivity and corrosion. J. Chem. Soc., pp. 478-492 (1930).

Chromic acid alone will produce passivity, so will sulfuric acid. Together they stimulate corrosion. Passivity thought to be due to presence of a film of salt of acid and iron.

Evans, U. R., - The passivity of metals, II. The breakdown of the protective film and the origin of corrosion currents. J. Chem. Soc., p. 92 (1929).

Corrosion starts at weak spots in the protective film, which is an oxide or hydroxide coating. "Differential aeration currents," which cause some electrolytic corrosion, are caused by differences of potential existing between places where the film is kept in repair by the presence of oxygen and other points where it is not kept in repair. E.M.F.'s due to this have been measured (approaching 0.5 volt) when no current was flowing. They fall off when current flows. Bending or scratching injures the film.

Fitzgerald, Charles, - Relation of pipe line currents tocorrosion. 12th Annual Meeting A.P.I. Proc. IV. (1931).

Pitting increases as resistivity decreases. Insulating coating on pipe at specially corrosive points reduces long line currents to nearly zero. Burying steel and zinc plates near the pipe and electrically connected to it causes a sharp cathodic change at that point. The effect is more marked with zinc than with steel.

Friend, J. N., - New theory of the corrosion of iron. Am. Electrochem. Soc. Trans., 40, 63-80 (1921).

An auto-colloid catalytic theory, which postulates corrosion as starting with the formation of colloidal ferrous hydroxide.

Friend, J. Newton, - Rusting of iron. J. Iron Steel Inst., 77, 5-32 (1908).

Claims that the rusting of iron is primarily the result of acid attack rather than of electrochemical nature, and that the hygroscopic nature of rust underlies its chemical action.

Friend, J. N., - Hammond, D. W., and Trobridge, G. W., - Influence of emulsoids on the rate of solution of iron. Am. Electrochem. Soc. Trans. 46, 283-296 (1924).

Presence of emulsoids or colloids exert a surprisingly large protective effect, except in cases of continuous agitation.

Fujihara, T., - Nature of the protective film of iron. Am. Electrochem. Soc. Trans. 49, 327 (1926).

The protective film consists of soluble ferrous hydroxide.

Fuller, T. S., - Experiments on the corrosion of iron and steel. Am. Electrochem. Soc. Trans. 39, 199-211 (1921).

Oxidation speeds up corrosion. Corrosion starts quite rapidly but presently slows down to a constant rate.

Gee, W. W. Haldane, - Electrolytic methods for preventing corrosion. Trans. Faraday Soc. 9, 115-24 (1913).

Suggests using a current to prevent corrosion of boilers. Cumberland method. Mentions the fact that Sir Humphrey Davey suggested use of "protectors" for the copper sheathing of ships by using more positive materials as "protectors" - in Transactions of the Royal Society for 1823-5. He found the method effective.

Gill, Stanley, - Advancement in corrosion prevention. Proc. 12th annual meeting A.P.I. Chicago, Nov. 9-11 (1931).

Chemical treatment and normalizing treatment of strained steel.

Gill, Stanley, and Robers, W. F., - Relation of long line currents to soil corrosion. Physica, 1, 194-204 (1931).

Claims that "long-line currents" is, in general, without influence on corrosion. The relation between soil resistivity and corrosion cannot be said to be reliable.

Hadfield, R. A., and Newbery, E., - The corrosion and electrical properties of steels. Proc. Roy. Soc. (London) (A) 93, 56, 7, (1916-1917).

The method of measuring the potential and overvoltage of a metal gives better results than the accelerated acid test. Considerable data on various alloys included.

Hale, A. J., and Foster, H. S., - Action of dilute solutions of acids, alkalies, and salts upon certain metals. J. Soc. Chem. Ind. 34, 464 (1915).

Metals studied were commercial zinc, cast and wrought iron, aluminum, lead, copper, tin, nickel.

Hambuechen, C., - An experimental study of the corrosion of iron under different conditions. Bull. Univ. of Wis. No. 42, Eng. Series, 2, 229-75 (1900).

In all cases strained iron was anodic (electropositive) to the unstrained iron, and hence more corrodible.

Hambuechen, Carl, - Some practical applications of overvoltage phenomena. Trans. Am. Electrochem. Soc. 18, pp. 91-95, 1910.

The overvoltage of the metal should be considered as a factor in corrosion.

Hanson, A. C., - Corrosion and protective films. Ind. & Eng. Chem. 22, 554 (1930).

Ferrous hydroxide film formed.

Hanson, H. H., and Lewis, W. K., - Method of testing the mutual corrosive effect of metals. Trans. Am. Electrochem. Soc. 22, 259-64, 1912.

Determine the relative effect of dissimilar metals on each other by measuring the depolarizing current.

Harker, G., and McNamara, J., - Electrolysis as a means of preventing the corrosion of iron and steel. J. Soc. Chem. Ind. 29, 1286 (1911).

Results of experiments using steel plates in solutions of acids, sea water, and tap water. Prevention was by the Cumberland method - tested in a sugar plant in Sydney, Australia.

Heyn, E., and Bauer, O., - The corrosion of iron in water and aqueous solutions. Mitteilungen aus dem Koniglichen Materialprufungsamt 26, 1-104 (1908).

Said to be the most comprehensive experimental study on corrosion up to 1917.

Jarrett, B. L., - Success of calorizing in oil refining. Oil & Gas J. 21, pp. 82-4, Nov. 9 (1922).

Physical properties of calorized material; rates of oxidation at high temperatures.

Johnston, J., - The mechanism of corrosion. Ind. Eng. Chem. 15, pp. 904-905 (1923).

A discussion of the action of films in corrosion.

Kintner, S. M., - Alternating current electrolysis. Elect. J. 2, pp. 668-673 (1905).

In a case of corrosion by an alternating current, part of the material removed when a spot is anodic may be replaced when the spot becomes cathodic.

Lambert, Bertram, - Electrolytic theory of the corrosion of iron. Trans. Faraday Soc. 9, 108-14 (1913).

Mention chemically induced passivity - brief resume of electrolytic theory.

Kuhn, R. J., - Galvanic corrosion of cast iron pipes. Ind. & Eng. Chem. 22, 335 (1930).

Use of potential tangent method for determination of electrolytic currents.

Kuhn, R. J., - Electrolysis and soil corrosion work in New Orleans. U. S. Bureau of Standards corrosion meeting, Washington, Nov. 6, 1930.

Description of methods and instruments for measurement of electrolytic currents.

Kuhn, R. J., - Corrosion of underground pipe lines and cathodic protection. U. S. Bureau of Standards Corrosion meeting, Mar. 30, 1933.

Summary of results on cathodic protection of pipe lines.

McAulay, A. L., and Bastow, S. H., - Electrical behaviour of surfaces of corroding iron. Chem. Soc. j., pp. 85-92, Jan. (1929).

Corrosion due to electrochemical action; differences of potential exist because of differential aeration. A condition of stability is attained, with the formation of a protective film. The time required for this varies with conditions.

If a current of .04 amp per cm^2 be passed between iron electrodes, there is no effect beyond a slight temporary polarization.

McCulloch, L., - Passivity and corrosion of iron. Am. Electrochem. Soc. Trans. 50, 379-390 (1926).

Certain results indicate that passivity is due to an oxide film, which is broken by a sufficient difference of potential.

McCollum, B., and Logan, K. H., - Electrolytic corrosion of iron in soils. U. S. Bureau of Standards, Tech. Paper, No. 25, 1913, 69 pp.

Describe certain experiments in which test pieces were subjected to self-corrosion and to electrolytic corrosion.

McKay, R. J., - Corrosion by electrolyte concentration cells. Trans. Am. Electrochem. Soc. 41, 201-11 (1922).

Effect of agitation on corrosion; it speeds it up by making more area anodic.

Mott, W. R., - Overvoltage as a factor in the corrosion of metals. Trans. Am. Electrochem. Soc. 15, 569-74, 1909.

The electrochemical theory of corrosion must consider overvoltage as one of its factors.

Philippi, W., - Electrolytic protection of steam boilers against scale and corrosion. Elec. W. 79, 47 (1922).

Use of wrought iron anodes at current density 2 mil. amps. per sq. ft.

Rawdon, H. S., and Krynitzky, A. T., - Notes on corrosion testing by different immersion methods. Am. Electrochem. Soc. Trans. 46, 359-86 (1924).

Test must be adapted to use of metal tested. Notes presence and effect of protective film.

Richardson, E. A., and L. T., - Corrosion of cast iron and its bearing upon the electrolytic theory of corrosion. Trans. Am. Electrochem. Soc. 31, 191-203 (1917).

Cast iron does not corrode as rapidly as would be expected from its impure state.

Richardson, W. D. - Gap between theory and practice in the production of corrosion-resisting iron and steel. Am. Electrochem. Soc. Trans. 39, 61-81 (1921).

Describes difficulty in drawing conclusions. Gives a few characteristics of corrosion-resisting materials.

Richardson, W. D., - Experiments on the corrosion of iron and steel. Chem. & Met. Eng. 23, 243-50 (1920). Am. Inst. Chem. Eng. 13, pt. 1, 169-263 (1920).

Corrosion found to increase with stirring and aeration. Gray cast iron seems most resistant, though this varies with treatment and make of iron. Rust spots are cathodic; bright spots anodic.

Richardson, W. D., - Solution of metals in acids as related to corrosion. Am. Electrochem. Soc. Trans. 38, 245-78 (1920).

Behavior of corrosion samples in presence of acids and catalytic agents.

Rogers, W. F., - Influence of oil in soil corrosion. Oil Weekly, 68, No. 9, p. 12 (1933).

The presence of oil speeds up corrosion of iron pipe imbedded in soil.

Rosa, E. B., and McCollum, B., - Electrolysis and its mitigation. U. S. Bur. Standards Tech. Paper, No. 52, pp. 95-102 (1915).

Corrosion of rails by electrolytic action.

Scott, Gordon N., - A.P.I. Pipe coating tests. Proc. A.P.I. Meeting Chicago, Nov. 9-12 (1931).

Detailed report of very exhaustive tests on various pipe coatings.

Shepard, E. R., - Pipe line currents and soil resistivity as indicators of local corrosive soil areas. U. S. Bur. Standards J. Research 6, 683-708 (1931).

Direct relation between soil resistivity and corrosion. Areas of higher resistivity are areas in which pipe collects current; it loses current (becames anodic) in areas of lower soil resistivity. This relation is quite consistent.

Siebel, E. P., - Pitting of iron, particularly pipe; its causes and possible preventives. Nat'l. Eng. 13, 192 (1909).

Pitting electrochemically formed - due to lack of homogeneity of pipe. Wrought iron better than steel pipe.

Speller, F. N., - Corrosion of metals as influenced by surface films. Mech. Eng. 51, 431-4 (1929). Excerpts Chem. & Met. Eng. 36, 85-7 (1929).

Believes in electrochemical theory and presence of protective film. Recommends test of material for each use to which it may be put.

Speller, F. N., - Film protection as a factor in corrosion. Am. Electrochem. Soc. Trans. 46, 225-240 (1924).

Films may be formed by adding certain reagents, such as sodium silicate or lime. Film is only one of several factors in corrosion.

Van Brunt, C., - Corrosion, apparent relation of protective film to microstructure. Ind. & Eng. Chem. 21, 352 (1929).

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Electrochemical theory of corrosion is definitely set forth for the first time.