CATHODIC PROTECTION OF METALS IN ICE PLANTS

By
Robert W. Warner
and
A. J. McCrocklin, Jr.

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The benefits of education and of useful knowledge, generally diffused through a community, are essential to the preservation of a free government.

Sam Houston

Cultivated mind is the guardian genius of Democracy, and while guided and controlled by virtue, the noblest attribute of man. It is the only dictator that freemen acknowledge, and the only security which freemen desire.

Mirabeau B. Lamar

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FOREWORD

Corrosion is one of the most persistent of the natural processes of disintegration. The result, commonly known as rust, when iron and steel are affected, is found about us on all sides. The annual cost to industry and to the nation in general is on the order of hundreds of millions of dollars.

The ice manufacturing industry is a particularly heavy sufferer on account of the use of salt brine as a freezing solution. Salt and moisture come in contact with much of the equipment in the plant and conditions usually are such that rapid corrosion occurs. While many efforts have been made to stop or retard this destructive action, the results have been only partially successful. Since recent theories indicate that corrosion is fundamentally of an electrolytic nature, it is immediately suggested that an electrical method of control should be possible.

During the past few years, the Bureau of Engineering Research at The University of Texas in coöperation with the Department of Electrical Engineering has been carrying on a study of the problem of corrosion in ice plants with the view of developing a method of electrical protection of the equipment which is most subject to destruction.

In carrying on this study, field tests and observations were made in a number of representative ice plants in the State of Texas. These results later were analyzed in comparison with those secured from the study of a small-scale, completely-controlled, ice plant erected in the laboratories of the University.

This bulletin gives the results of the research to date and outlines a workable method of electrical or cathodic protection suitable for application in an ice plant in normal operation.

The work was started under the direction of Joseph W. Ramsay, late professor of electrical engineering at The University of Texas. It has been encouraged and materially aided by the Southwest Ice Manufacturer's Association under the leadership of L. P. Reiss of Marshall, Texas. The operators of the ice plants that were visited furnished whole hearted coöperation at all times. The authors wish to express their fullest appreciation for all this assistance. They also are indebted to Dean W. R. Woolrich of the College of Engineering and Director of the Bureau of Engineering Research for many helpful suggestions.

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CONTENTS

	PA	GE
Forew	ord	3
I.	Summary of Results	7
II.	Introduction	7
III.	Theory of Corrosion	9
IV.	Factors Affecting Corrosion	11
V.	Theory of Cathodic Protection	12
VI.	Plant Tests	14
VII.	Preliminary Field Investigation	15
VIII.	Laboratory Studies	18
IX.	Results of Laboratory Investigation	21
X.	Comparison of Field and Laboratory Tests	25
XI.	Conclusions	25
XII.	Summary of Recommendations on Ice Plant Corrosion by Cathodic	
	Protection	30

LIST OF FIGURES

Figuri	E PA	AGE
1.	Battery couple showing flow of current between two spots on the same piece of metal when in contact with an electrolyte	9
2.	Elementary battery formed by two dissimilar metals in contact with an electrolyte. Current flow is shown	10
3.	Protecting circuit showing external source of current, replaceable anode and current flow toward ice cans and ammonia pipes	13
4.	Potentiometer circuit for measuring potentials in brine tanks	15
5.	Variation of the voltage of an ice can after being filled with fresh water	17
6.	Electrical connections for supplying protecting current to cans, coils and tank in small-scale laboratory ice plant. Connections to measuring potentiometer also are shown	19
7.	Blisters appearing at random on the surface of cans due to unsuitable film composition or excessive thickness	20
8.	Variation of protecting voltage at the surface of ice cans due to protecting current at different brine temperatures in the laboratory plant, using 50-pound cans having 7 square feet of surface area	21
9.	Variation of current-density with brine temperature necessary to maintain protecting voltages at the surface of ice cans	22
10.	Variation of current-density with brine temperature necessary to maintain protecting voltage at the surface of brine tank and ammonia pipes	23
11.	Relations between protecting voltage, time after refilling, protecting current and specific gravity of the brine	24
12.	Showing the effect of treating brine with chromates. Protecting current versus time for protecting voltage of —0.4 volts	25

CATHODIC PROTECTION OF METALS IN ICE PLANTS

I. SUMMARY OF RESULTS

The first step in this research was a thorough study of the mechanism of corrosion in tanks used for freezing ice. This resulted in the development of special precision measuring instruments for investigating the electrical conditions accompanying corrosion. Field tests were made using this equipment in ice plants in regular operation, the results of which are given in this bulletin.

In order to be able to make observations close at hand and under a wide variety of readily controlled conditions, a miniature ice plant was constructed in the laboratory of the Bureau. Here the brine temperature, gravity, acidity and rate of flow could be controlled at will. Exhaustive tests were made on this plant and much valuable data were secured. These are shown in the form of curves. From these tests it was found that if an electric current of the correct amount and direction were passed through the plant, corrosion would be prevented, thus indicating that the electric current was acting as a protecting agent.

The same method later was tried in an actual ice plant with similar results. The current density used and all other details are given in the bulletin following.

II. INTRODUCTION

Usual Ice Plant Conditions

The principal parts of the ice freezing plant are a large tank containing a salt brine solution, and immersed in the brine, pipe coils carrying ammonia to reduce the liquid to a freezing temperature of from 10° F. to 25° F., and cans containing fresh water to be frozen into commercial ice. Other equipment consists of compressors, pumps, brine circulating propellers, piping and the like.

Practically all of this equipment is of iron or steel and readily subject to corrosion, which is usually evidenced by the familiar pitting and scaling of the surfaces. The tank is usually of material thick enough so that in spite of corrosion leaks are not frequent. However, when they do appear, replacement of the tank or expensive repairs are necessary.

Ammonia coils consisting of pipe and fittings are heavy sufferers from corrosion. The pipe is usually of steel and if the fittings are cast iron an action is set up whereby the metallic iron is removed from the fitting leaving mainly the carbon. The result is a graphite-like substance easily cut with a knife and likely to break at the slightest strain. If the joints are welded, action frequently results from the contact of the dissimilar metals of the pipe fitting and welding rod used, with the result that wholesale corrosion frequently makes replacement necessary long before the end of their normal useful life.

The freezing cans are the parts most seriously affected by corrosion. They are of necessity made of thin material and must be galvanized, at least on

the inside, to keep the water and ice in them clear. Even the smallest hole in a can destroys its usefulness. Corrosion frequently reduces the life of these cans to 6 or 8 years or to about one-third of what might be expected of them.

Practice varies in the way the ammonia coils or pipes are placed in the tank and there is considerable variation in the methods of supporting and handling the cans. In some plants the ammonia pipes are placed between each row of cans while in others they are grouped together at the ends or sides of the tank. The brine is made to circulate by motor-driven propellers so as to maintain a fairly uniform temperature throughout the tank. In some plants the cans are handled singly while in others they are fastened together by brackets in groups. Frequently the individual cans are arranged to float in the brine or rest on strips of wood placed on the bottom of the tank. In other plants the cans rest on metal brackets supported from the framework of the operating floor above the tank, or are suspended from brackets tying groups of cans together.

These differences in construction do not materially seem to affect the prevalence of corrosion. While it is frequently much worse in some plants than in others, the type of construction or arrangement of parts does not seem to be responsible to any considerable extent. Other causes apparently must account for it.

Methods of Control

Various chemical methods for preventing or reducing corrosion in brine tanks have been attempted for years. These are expensive and have been only partly successful. In the main, they consist of adding certain chemical compounds to the brine with the hope that they will come sufficiently into contact with the exposed surface of the cans, coils and tank to form in some fashion a protective coating upon them. Chromates, chromic acid, phosphates, silicates and other compounds have been used with varying degrees of success.

The chief action of these rust inhibitors seems to be the formation of a viscous layer or film of material covering the metals submerged in the brine solution. The formation of such a film is correct in the theory of corrosion prevention but the films produced by the chemicals usually used are so thin that the brine penetrates and corrosion is by no means entirely prevented. Such inhibitors do tend to reduce the natural potential exhibited between the metal and brine and to this extent no doubt do reduce corrosion. In general, paints consisting of tar or rubber compounds are not practical because they retard the flow of heat from can to brine and ammonia coils. It is upon this flow of heat that the freezing action depends. In addition, some paints have a tendency to crack or to develop minute holes in them and at such spots corrosion is greatly accelerated.

Electrical or cathodic protection has been applied commercially in many places, notably for the preservation of pipe lines buried in the earth or extending through water, especially sea water. Here the method has been quite successful in retarding or stopping corrosion completely and economically has been the means of saving tremendous expense.

III. THEORY OF CORROSION

In order to explain the action of the cathodic method of corrosion control, a short review of the electrolytic theory of corrosion is necessary. Originally it was thought that corrosion resulted from the direct combination of oxygen with metal. However, this theory did not account for corrosion under many conditions so that when more information was obtained about the action of electrons and ions in solutions, it was realized that the original theory was quite inadequate.

According to the electrolytic theory, corrosion occurs when the metal or metals involved are in direct contact with an electrolyte. This electrolyte may be in the form of an acid or alkali solution, moist earth, plain water, or simply moisture in the air. Resulting from this contact, a difference of electric potential, or voltage, is set up between any two metals that may be present, or even between two spots on the same piece of metal. Several things may give rise to such difference of potential. One of the most common is unlike chemical composition or a difference in molecular structure. It also may be due to internal molecular strains or to differences in temperature between two parts of the same piece of metal. On account of this condition, a small electric battery is formed and since the body of the metal itself short circuits this battery voltage, a minute electric current flows continuously. This is shown diagramatically in Figure 1. Figure 2 shows the same situation when two different metals are involved.

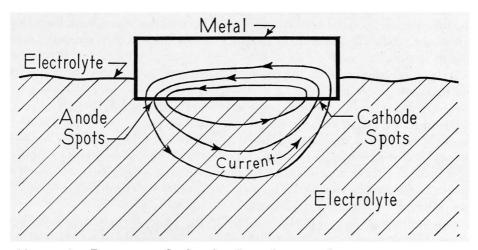


Figure 1.—Battery couple showing flow of current between two spots on the same piece of metal when in contact with an electrolyte.

Electric current is believed to consist of the flow of electrons at a certain rate through a circuit and if these electrons move through an electrolyte from one metal to another or from one spot on a piece of metal to another spot, some of the metal itself is converted into the ionized form.

An ion is a molecule that has lost one or more electrons and is therefore positively charged. These minute particles in the form of ions are permanently

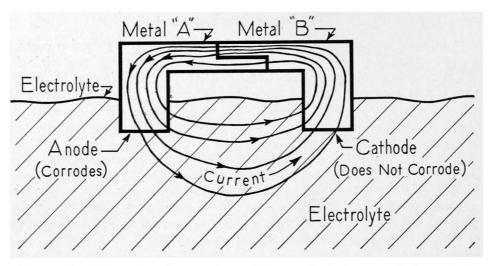


Figure 2.—Elementary battery formed by two dissimilar metals in contact with an electrolyte. Current flow is shown.

detached from the original metal and pass into the electrolyte. In most cases, they finally combine with oxygen and other elements to form oxides, hydroxides, salts or complex compounds. In the case of iron or steel, the oxide formed is known as common rust.

This action occurs only at places where the electric current *leaves* the metal to enter the electrolyte because it is here only that the metal ions mentioned above are produced. The metal at this point in the electric circuit is known as the "anode."

At the opposite side of the circuit where the electric current leaves the electrolyte to *enter* the metal, a somewhat reversed process takes place. If there are metal ions of the right type in contact with the metal itself, they are changed to the metallic form and are deposited or plated upon the metal. A familiar example of this action is the well known commercial process, whereby metals such as silver, copper, nickle and others may be removed from a solution of the salts of these same metals and plated upon another metal solely by the action of the electric current. The metal or spot where current thus leaves the electrolyte is known as the "cathode."

Chemically, this process is expressed by the equation $Me^{\circ} \longrightarrow Me^{n(+)} + n^{(-)}$ where Me° represents any metal in its original or metallic state. $Me^{n(+)}$ represents an atom of this same metal in the ionized state wherein it has lost n electrons designated by $n^{(-)}$. The term $Me^{n(+)}$ represents the particle of the metal that is detached from the original surface ultimately to combine with oxygen or other elements and give evidence of corrosion. The reverse or plating action is represented by the equation $Me^{n(+)} + n^{(-)} \longrightarrow Me^{\circ}$.

Finally, corrosion will take place at all points or spots that are "anodic" but will not occur at places which are "cathodic." This fact gives rise to the name of this electrical or electrolytic method of corrosion control.

IV. FACTORS AFFECTING CORROSION

According to the electrolytic theory, corrosion is due to the electrolytic transfer of metal accompanying the flow of electric current through a solution which is in contact with the metal. In order for current to flow, it is necessary that there be a difference of potential between the points of flow.

Metal Potentials

Every metal exhibits a natural potential with respect to an electrolyte, which is any solution capable of carrying an electric current. Moist earth, even, may serve as an electrolyte. The value of this potential depends upon the temperature of the electrolyte, temperature of the metal, concentration of the electrolyte, kind of metal, kind of electrolyte and the molecular condition of the metal; i.e. whether annealed or under strain.

In the ice plant, iron or steel ice cans, and ammonia coils are submerged in a solution of salt contained in the large steel tank. The salt solution forms a convenient electrolyte for any current that may flow in response to such differences of potential or voltages set up between the parts of the system. The iron or steel at all points has a natural potential with respect to the brine and if any condition causes this potential to be higher at one spot than at another, an electric battery or "battery couple" is formed and, if a return path exists, current will flow between those points. The return path is provided by the body of metal, which in effect short-circuits the battery. This condition also is illustrated in Figures 1 and 2.

Effect of Temperature

Difference in temperature causes a difference of potential. If the bottom of an ice can is colder than the top, current will flow in the brine from top to bottom and in the metallic wall of the can from bottom to top, thus completing the electric circuit. Due to the circulation of the brine a difference of temperature will exist between various sections of the ammonia coil system. Current will flow between such points. The velocity of the circulating brine also may affect the amount of potential difference between parts of the system, although this may simply be related to the temperature gradient.

Metal Conditions in Ice Plants

If unrelieved stresses exist in any parts of the ammonia coil system, such as at welded joints, battery couples are formed Welds are particularly subject to corrosion if the composition of the welding rod was not the same as that of the metals welded together. A condition frequently found in ice plants which greatly favors corrosion is the use of metals which are naturally quite unlike in contact with each other. Cast iron fittings on steel pipe is an example. Brass in contact with iron or steel is always conducive to corrosion and brass air tubes frequently are attached to the galvanized sides of ice cans. Bronze impeller wheels often are placed on iron shafts of circulating pumps.

If any two unlike metals are in contact with each other under the brine, a battery couple is formed and current will flow.

Riveted joints and seams in ice cans frequently are wiped with solder, an alloy of lead and tin. The resulting potential difference is short-circuited by some metallic part so that current flows constantly with accompanying corrosion.

Brine Solution pH Value

A very important factor in the rapidity of corrosion is the degree of acidity or alkalinity of the brine solution. This is indicated by the concentration of the hydrogen ion in the solution as expressed by the symbol pH. A pH value of 7.0 denotes a neutral solution. A value above this indicates that the brine is alkaline, while one below 7.0 means that the brine is acid. Values of pH from 7.0 to 8.2 result in minimum differences of potential and minimum changes in conductivity of the electrolyte with consequently the least tendency to corrosion.

V. THEORY OF CATHODIC PROTECTION

According to the electrolytic theory of corrosion, natural potentials which are set up between metals and parts of metallic equipment when in contact with an electrolyte cause minute electric currents to flow. Wherever these currents flow away from a spot on a piece of metal and enter the electrolyte, disintegration or corrosion takes place at the spot and the extent or rapidity of such corrosion is proportional to the density of this current.

Knowledge of this electrolytic process at once suggests the possibility of devising an electrical remedy. If the minute batteries within the system could be overcome and the electrical current stopped or forced to flow only in the correct direction, corrosion would be prevented. It is relatively easy to do this and the method of "cathodic protection" depends upon the control of this internal current. It is necessary only to provide an external source of electrical energy and the flow of current within the system is thereby brought almost entirely under the regulation of the operator.

It should be noted that it is unnecessary to reverse the natural potentials between metal and electrolyte or between metals in order to accomplish protection. The natural current flow may be reversed but the natural potentials are lowered only somewhat in proportion to the current sent into the system. This action is readily understood by reference to the ordinary storage battery. Under discharge, current flows away from the positive terminal into the external circuit. When the battery is charged, current is sent into the battery at the positive terminal. The current is reversed but the polarity remains unchanged.

Cathodic protection, then, depends upon forcing current to *enter* all metals and surfaces it is desired to protect—that is, forcing them to become electrolytic cathodes. The amount of voltage by which the natural potentials are lowered as a result of this current flow is known as the "protecting voltage." It

depends upon a number of conditions as well as upon the amount of current flowing and will be discussed later.

It is necessary to complete the electrical circuit and in order to provide a point where the current will harmlessly enter the electrolyte, an artificial anode must be provided. This may consist of any piece of metal submerged in the electrolyte—something that is inexpensive, replaceable and of suitable composition. All of the corrosion of the system then will be centered at this replaceable anode. This is illustrated in Figure 3, which shows current leaving the anode, flowing through the brine and entering the ammonia pipes and cans in the ice plant.

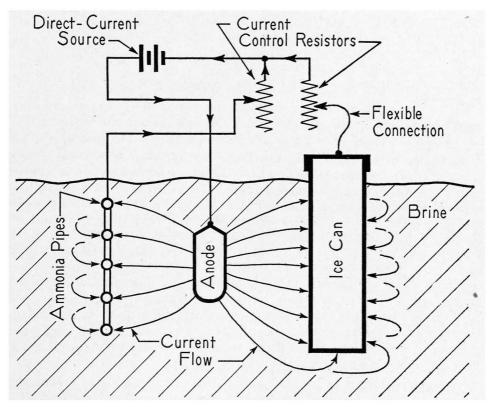


Figure 3.—Protecting circuit showing external source of current, replaceable anode and current flow toward ice cans and ammonia pipes.

Surface Films

The electrolyte in the ice plant is a liquid, salt solution, therefore the positively charged metal ions detached from the anode are free to travel over to the cathode under the influence of the current. Here they become neutralized and are deposited in the form of a semi-liquid film on the surface being protected. Some metals if used as anodes in electrolytes will form objectionable films. The safest rule is to use a metal that is more active than the one to be protected. Chemically, this film is of the nature of a complex hydroxide of

the metal which is used as the anode and its presence on the surface of the cathode is the best evidence that the system of protection is functioning properly.

Even if the protecting current is stopped, this film by itself will furnish protection for a short time—probably for several days. After that the film becomes dissolved by the brine and conditions favoring corrosion return.

In the light of the foregoing theory, the action of chemical corrosion inhibitors is further explained. They form a thin chemical film on the surface of metals under the electrolyte and this film reduces the natural potentials exhibited by the metals to the brine and between the metals themselves. In turn, the internal current is lowered and corrosion is reduced correspondingly.

This electrolytic protecting film is deposited over every minute spot on the surface of the metal being protected. The electrical resistance of the metal to brine is so low that the current distribution is essentially uniform. This means that the protecting film will tend to be formed with practically uniform distribution regardless of the concentration of flow of the brine.

For various practical reasons, complete elimination of corrosion frequently cannot be secured by cathodic protection, although the amount of destruction can readily be reduced to only a small fraction of what would otherwise occur.

VI. PLANT TESTS

In order to apply cathodic protection, it is necessary to investigate and determine carefully the voltage conditions existing throughout the plant. The rapidity and seriousness of corrosion can be judged by inspection and by examination of plant records as to the frequency of replacements and repairs in the past. Determinations of pH values can be made by the usual comparative tests which are familiar to all plant operators. Temperature measurements, and gradients can readily be made, although usually, they are not particularly significant. Most important are the differences of potential or voltages that exist between the various parts such as coils, cans and tank. The presence of such voltages is proof that corrosion probably is taking place and their magnitude is a measure of its rapidity.

Voltages existing in an ice tank are relatively small compared to ordinary commercial values, being on the order of thousandths of volts or millivolts. An ordinary millivoltmeter cannot be used directly to measure these voltages because the batteries that give rise to them have capacities too low to operate commercial meters. Therefore, a method must be used which takes no current from these minute cells. Such a scheme is known as a "null method."

One of the most accurate instruments suitable for such measurements is the electron potentiometer. One of these built in the electrical engineering laboratory was used for comparative measurements. However, this is a device much too delicate for ordinary field work and a more simple type of potentiometer is generally quite satisfactory. It can be purchased as a unit or set up with easily obtained parts. In effect, it consists of an ordinary 1.5-volt storage

battery, a slide-wire resistor, a portable galvanometer, a variable-range, low-reading voltmeter, a key and reversing switch. This is shown in Figure 4.

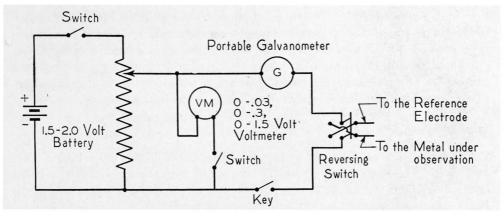


FIGURE 4.—Potentiometer circuit for measuring potentials in brine tanks.

The slide-wire resistor is connected across the 1.5 volt-battery with a switch for convenience in disconnecting when not in use. Voltages from points in the ice plant system are then balanced against a part of the voltage drop across the slide-wire resistor. When an exact balance is reached, the galvanometer will give no deflection when the key is depressed and the voltage across that portion of the resistor used is then read with an ordinary millivoltmeter. Voltages usually found range from 200 millivolts positive to around 500 millivolts negative. A reversing switch is used to avoid having to take time to change connections in case the meter happens to be reversed and does not read up scale.

Apparatus of this kind is rugged and readily portable. With it a complete voltage survey of a plant can be made within a few hours. It is best to measure all voltages with reference to some convenient point which may be ammonia coils, outside tank or an external water main.

VII. PRELIMINARY FIELD INVESTIGATION

Ice Plants Examined

Early in this investigation of corrosion, a number of ice plants in Texas were visited and a complete survey made of the conditions existing in them. These plants were located in Austin, Boerne, Carthage, Center, Floresville, Henderson, Longview, Marshall, Mt. Pleasant and Seguin. All were experiencing the usual troubles with corrosion. Ice cans were failing after much less than normal life, condenser tubes were developing leaks, evaporator coils were badly pitted and had developed leaks. Agitator shafts were causing trouble. Bolts used in construction under the brine often failed. Ice cans showed bad corrosion at the brine line, in corners and at seams. It was found that new cans placed in a tank along with old ones frequently experienced

very rapid corrosion, sometimes failing at the seams in less than a year after being placed in service.

These plants visited were largely typical in their general form of construction and arrangement of freezing equipment. Some used high- and some low-pressure air agitation. In some plants, the ammonia coils ran between the rows of cans, while in others, the coils were arranged in a bank and the brine circulated rapidly to maintain approximately uniform temperature throughout the tank. The ice cans were either floating or suspended in grids. In some places they were attached together in gangs of from four to twenty.

Different Metals Used

Frequently, several different metals would be found in the same tank. The main brine tank was usually of steel. Ice cans of steel were galvanized within and without and the seams fastened with iron rivets and the joints soldered. Brass air pipes frequently were found brazed to the side of the can. Ammonia coils of steel were joined with wrought or cast iron fittings. Sometimes the pipes were welded together. The brine circulating impellers were usually of bronze fitted to a steel shaft.

This mixture of metals is particularly bad because all of them have different natural potentials to the brine solution and thus form the poles of many batteries, of which the brine is the electrolyte, which send currents in all directions throughout the system.

Voltage Conditions Found

Exhaustive voltage tests were made in the course of these plant surveys to determine the electrical relations of the various pieces and parts of the system and a wide variety of conditions was observed. All sorts of voltage relations existed. Ice cans in the same tank registered a potential difference of as much as 600 millivolts between them. Some cans were positive with reference to the ammonia coils while others in the same tank were negative. Such conditions existed usually where the cans were supported individually and fairly well insulated from one another. Where the cans were tied together by metal grids or held in metal frames, the potential differences between the cans in the tank were quite low. They would be zero if the contact were good enough. In some cases, new cans indicated considerable voltage with respect to the ammonia coils while older cans in the same group were at a much lower potential difference, probably due to the zinc coating on the former. This explains why new cans frequently suffer more corrosion than old ones. As might be expected, the tank, agitator and ammonia coils were at practically the same potential due to their being in direct contact at several places.

Temperature Differences Affect Voltage

It was noted that the difference of temperature in the brine stream was accompanied by a difference of potential of some 50 millivolts between cans

and coils. Cans in the colder spots were more negative to the coils than those in the warmer places.

Another effect of temperature difference was observed in the gradient from top to bottom of the ice can. This gave rise to a difference of potential between top and bottom of the can of as much as 15 millivolts. The metal of the can itself short circuits this voltage, and the resulting current flow is responsible for constant corrosion. This same condition tends to exist along the sides of the brine tank itself and along the ammonia coils and headers.

A still more important effect of temperature on the voltage between ice cans and ammonia coils was observed immediately after filling a can with fresh water and replacing it in the brine. This voltage was observed to vary as much as 120 millivolts, starting at 100 millivolts positive and changing to 20 millivolts negative by the time the water in the can was completely frozen. The rate of this change is shown in Figure 5. This is significant in that it indicates, to a degree at least, a condition favorable to corrosion every time a can is emptied and filled.

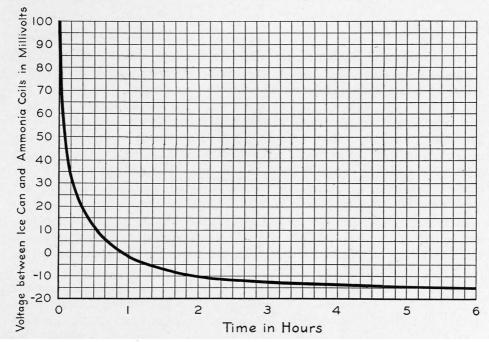


FIGURE 5.—Variation of the voltage of an ice can after being filled with fresh water.

Corrosion at Brine Line

Nearly all ice cans showed bad corrosion at the brine line. Surface conditions change very rapidly between points a few inches above the brine line and a few inches below the line. The oxygen entrapped in the moisture above the brine and in the brine itself along the surface of the can has considerable

effect on the battery couple formed at the brine line and tends to increase the difference of potential present.

Effect of Chemical Treatment

Treatment of the brine in general affected the voltage observed between ice cans and ammonia coils. When untreated brine was used, the voltage between cans and coils averaged approximately 250 millivolts, whereas with treated brine the voltage averaged around 180 millivolts. Corrosion is automatically reduced by such a reduction of voltage.

VIII. LABORATORY STUDIES

Any tests in the field are subject to interruption due to the necessary operation of the plant while the study is being made. Therefore, it was decided to construct a small-scale ice plant in the laboratory at The University of Texas so that all conditions could be held under control while measurements were being made and the results observed.

Miniature Ice Plant

This small-scale, laboratory, ice plant consisted of a cork-insulated tank, ammonia coils, eight 50-pound cans and brine agitator. The tank measured 4 feet by 4 feet by 3 feet deep. There were positions for nine ice cans but one in the center was removed to make room for the brine agitator. The cans were a standard, 50-pound size, galvanized inside and out, with riveted and soldered seams. They were arranged so as not to make contact with each other or with the ammonia pipes or with the tank itself. The ammonia pipes were arranged vertically between the cans. The agitator forced a flow of the brine downward in the center of the tank and a variable-pitch, variable-speed propeller made it possible to regulate the circulation at will.

A Honneywell temperature control made it possible to regulate the temperature to within approximately one degree Fahrenheit and an Alcove expansion valve was used to control the ammonia. In this way, the operation of the plant was made completely automatic.

Electrical connections were brought out from the tank, ammonia pipes and each can, and were carried to a central control board with measuring panel so that all voltages could be read quickly and accurately.

Ordinary city water with ice-cream salt made up the brine solution. No chemical corrosion inhibitors were added. Values of pH ran from 7.0 to 9.0. Sodium hydroxide was added to the brine when higher values of pH were wanted and hydrochloric acid was used to get lower values.

Method of Investigation

Some measurements were made with clear water in the cans and others with the water completely frozen. Several values of pH were tried and dif-

ferent brine temperatures, brine concentrations, and several degrees of agitation.

In each case, the plant was operated until the relations within the tank had become stable and then all the voltages between the cans, coils and tank were measured. After this was completed, cathodic protection was applied and the tests repeated.

Protecting voltage and current of the desired value were obtained, first from storage batteries and later from a copper-oxide rectifier supplied from a 60-cycle, alternating-current line. Either source proved to be entirely satisfactory. The electrical connections are shown in Figure 6.

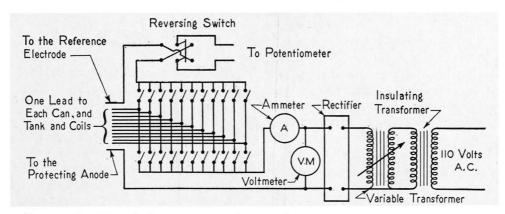


FIGURE 6.—Electrical connections for supplying protecting current to cans, coils and tank in small-scale laboratory ice plant. Connections to measuring potentiometer also are shown.

Anode Material

Several materials were tried for the protecting anode, where the electric current entered the system. Carbon, cast iron, lead, aluminum and zinc were used with varying results. For several reasons outlined later, zinc proved to be the most satisfactory.

At the anode, positively charged metal ions are released and gradually move over to the cathode where they combine with electrons to become metallic again and in so doing, produce a film covering every particle of the surface.

The material of which the anode is composed is extremely important because upon it in a large measure depends the effectiveness of the whole process of protection. It should be reasonably free from impurities and must be obtainable readily and cheaply for practical and economic reasons.

Protective Film

The film produced on the surface of the cathode must be of suitable thickness and density. If too thick and heavy, unnecessary electrical resistance will be introduced into the circuit and corrosion will take place beneath the film. This would be indicated by the formation of blisters on the surface of the cathode.

In the laboratory tests, cast iron, scrap steel, and lead were tried as anode material but blisters formed on the surface of the cans in each case showing that they were not suitable. These appeared as shown in Figure 7. Carbon was not suitable because of the formation of chlorine gas with it. Aluminum and zinc proved to be more satisfactory and especially zinc. The film formed with it remained intact and furnished protection for several days after the electric current had been cut off.

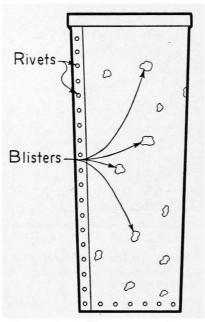


FIGURE 7.—Blisters appearing at random on the surface of cans due to unsuitable film composition or excessive thickness.

At the same time the protective film was being formed on the surfaces of the laboratory plant, an objectionable film also accumulated on the surface of the zinc anode. This appeared to be composed of colloidal particles that had been in suspension in the brine and was overcome by suspending the zinc in a fine-meshed cotton bag such as an ordinary sugar or salt bag. This bag also prevented impurities in the zinc and small particles of zinc itself from falling to the bottom of the tank.

The film formed from zinc is of a grayish color and although it covers the surface of the cans closely and completely, is of a watery constituency and can easily be rubbed off. However, this is not apt to happen in regular operation. The presence of a good film is positive assurance that the protective scheme is working effectively.

IX. RESULTS OF LABORATORY INVESTIGATION

A number of significant facts and relations were determined in the course of the work with the ice plant in the laboratory.

Anode Material

One of the most important of these was the fact that of the common and most readily obtainable materials, zinc is the most suitable for the artificial anode. In normal times, zinc is relatively inexpensive and easy to secure. In addition, the protecting voltage necessary with a zinc anode was found to be considerably lower than that necessary with the other materials.

Protecting Voltage

The amount of protecting voltage must be sufficient to offset all of the changes in voltage that occur among cans, coils and tank in the normal cycle of operation of the plant. It must also be enough to insure that the surfaces being protected are sufficiently negative with respect to the other parts of the system. Only under such conditions will the current flow be able to furnish ample protection and only under these conditions will the protecting film be formed on the surfaces it is desired to protect. Usually a protecting voltage of from 200 to 400 millivolts, negative, is sufficient.

Effect of Brine Temperature

Temperature of the brine has a marked effect on the current-protecting voltage relations as is shown in Figure 8. The negative sign of the voltage

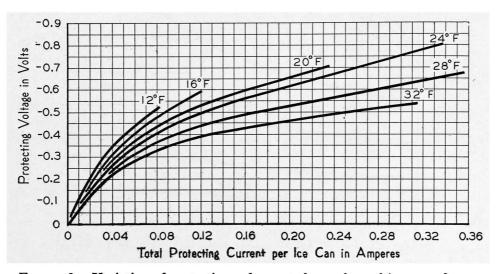


Figure 8.—Variation of protecting voltage at the surface of ice cans due to protecting current at different brine temperatures in the laboratory plant, using 50-pound cans having 7 square feet of surface area.

indicates that the original voltage without protection was reduced, made more negative, by that amount when cathodic protection was applied. As the temperature of the brine decreases, a higher protecting voltage results from a given current density. In other words, for lower brine temperature less current should be necessary to secure a given degree of protection. These relations are not linear, probably due to the electrical characteristics of the protecting film. The temperature-resistance characteristics of the brine also affect these relations to some extent.

In Figure 9 are shown the relations between current density in milliamperes per square foot of can surface and brine temperature for several values of

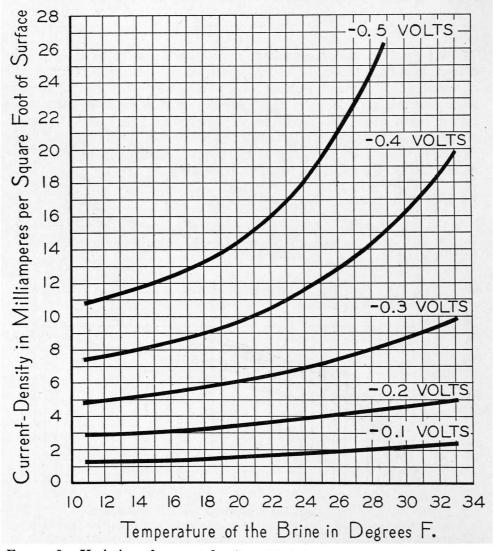


Figure 9.—Variation of current-density with brine temperature necessary to maintain protecting voltages at the surface of ice cans.

protecting voltages. Figure 10 shows the same relations for tank and evaporator coils. It can be seen that the difference in current density necessary to provide a given protecting voltage is not great.

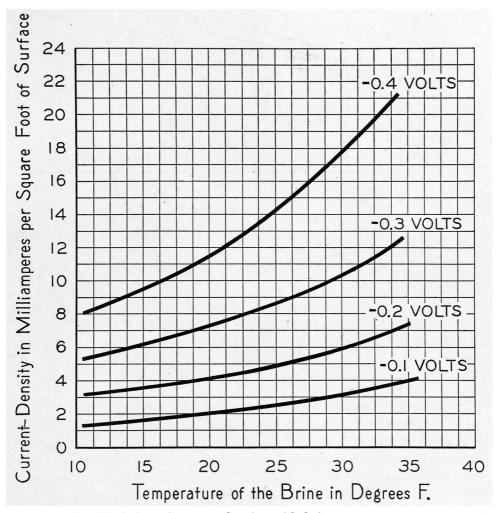


Figure 10.—Variation of current-density with brine temperature necessary to maintain protecting voltage at the surfaces of brine tank and ammonia pipes.

These curves are useful in determining the amount of current necessary for protection when the temperature of the brine is known.

Effect of Brine Density

Specific gravity of the brine is another factor in the relations between protecting voltage, current and time. These are shown in Figure 11 and, again it is seen that with lower specific gravity, stable conditions after refilling are reached somewhat quicker than with brine of higher specific gravity.

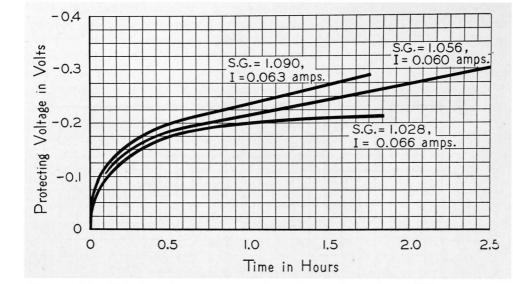


Figure 11.—Relations between protecting voltage, time after refilling, protecting current and specific gravity of the brine.

Effect of pH

Variation of pH values between 7.0 and 8.5 have very little effect upon the current and voltage relations. However, for values of pH above 8.5, the current necessary for a given protecting voltage increases rapidly.

Effect of Time

The value of protecting voltage secured with the flow of a given current varies also with time. It was shown in Figure 5 that with a given current the amount of protecting voltage required decreases with time, it being from one and one-half to two hours after filling a can with fresh water before stable conditions again are reached. This curve indicates that without an enduring protective film on the surface of the can there would exist a considerable gap in the protection every time the ice is taken from a can and it is refilled with water and replaced in the brine for freezing.

Effect of Chromate Treatment

Chromates added to the brine also produce a certain amount of protecting film on the metal surfaces beneath the brine. Such film seems to assist the electrolytic film formed by the electric current and its effect is indicated by the curves of Figure 12. It is seen that considerably less current would be required for adequate cathodic protection if the brine were treated.

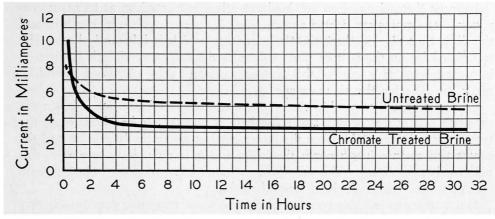


Figure 12.—Showing the effect of treating brine with chromates. Protecting current versus time for a protecting voltage of -0.4 volts.

X. COMPARISON OF FIELD AND LABORATORY TESTS

After the studies in the laboratory plant were completed, the same method of cathodic protection was applied in a commercial ice plant in regular operation. In general, the results agreed closely with those found in the laboratory. In some cases, current densities 10 or 15 per cent lower than those used in the laboratory were sufficient to provide a satisfactory protecting voltage.

Many cans showed the characteristic blisters due to unfavorable surface conditions with consequent active corrosion. On such cans the dark hydroxide protecting film was quickly formed when current was applied showing that the method would fully be effective in reducing or preventing corrosion.

XI. CONCLUSIONS

From the foregoing, it would appear that protection of the cans, ammonia coils and tank in an ice plant against corrosion by the method of cathodic protection is entirely feasible and should be quite effective if applied properly and consistently.

Basic Precautions

Corrosion occurs almost everywhere in the ice plant so that every possible care should be taken in controlling it. All conditions that inherently favor corrosion should carefully be avoided. The use of different metals in contact with each other should not be permitted. Brass air pipes on steel cans should not be used. Brass fittings on steel or iron pipe promote corrosion. Even the use of cast iron fittings with wrought iron or steel pipe is a bad practice. Welded joints are much better but the welding rod must be very similar to the pipe in composition or electrolytic action will take place at the weld and cause it to fail within a few years.

Ice cans themselves often are inadvertantly constructed so as to favor corrosion. The seams are riveted and the joint is covered with solder, a lead and tin alloy, thus placing three metals in contact, which is inherently bad. The standing joint on the bottom traps air under the can every time it is lowered into the brine. If a joint of this type is necessary, some provision should be made for allowing the air to escape.

One of the most vulnerable places on the can is at the brine line. Frequently cans fail first at this point. Corrosion here is particularly bad because of the temperature difference between the moist can just above the brine line and the submerged surface just beneath the brine and it is difficult to overcome this unfavorable condition. The use of an asphaltic paint of some nature around the top of the can might be of some benefit.

Galvanizing on a can seems to be of little value against corrosion. It may serve to keep the water and ice inside the can clear but on the outside, it disappears so quickly that it would seem to be quite worthless. The metallic film of zinc hydroxide formed on the surface of the cans under cathodic protection is permanent as long as the method is correctly applied and is far more effective than any galvanizing.

Without doubt there is considerable merit in many of the various chemical treatments applicable to the brine. It was shown above that the amount of current necessary for cathodic protection would be reduced if the brine were chemically treated. Therefore, it would seem logical to consider using chemical treatment in addition to electrical protection.

There is always a possibility that stray earth currents from outside sources of direct current may pass through the tank, since it is usually in more or less direct contact with the earth. Wherever current happens to leave the tank for the earth, corrosion will be particularly bad. To prevent this, the tank should be thoroughly grounded to a water main or else to an artificial ground made of large junk castings buried in the earth and kept moist. In some cases it might be advisable also to ground the evaporator coils.

Protecting Voltage Necessary

A protecting voltage of between 200 and 400 millivolts, negative, is usually enough to counterbalance all the variations in voltage from time to time due to changes of brine temperature and specific gravity. This voltage also is usually sufficient to hold all the metals it is desired to protect at a potential low enough to insure that current will flow only toward them under the surface of the brine. Voltage variations may be determined by means of the potentiometer circuit shown in Figure 4 where the tank itself is used as a reference level. Such measurements will not give the voltage of the cans or coils to the brine but will indicate the order of the protecting voltage necessary.

Potential Measurements

It is frequently helpful in applying cathodic protection to have some idea of the potential of the ice cans and ammonia pipes with respect to the brine itself. This can readily be measured by means of the circuit in Figure 4 using a reference electrode immersed directly in the brine.

A small piece of sheet platinum or platinum wire will serve for such an electrode. The junction between the platinum and a copper lead to the measuring apparatus must be kept perfectly dry or an additional, unwanted voltage will be introduced and spoil the results. To do this, it is best to seal the platinum into the end of a glass tube. The junction between the copper and platinum should be welded and also placed within the glass tube which should be filled with paraffin to keep out moisture. The outside of the glass tube should be kept perfectly dry.

A piece of carbon from an ordinary No. 6 dry battery also will serve reasonably well as a reference electrode. In order to keep the junction between carbon and copper lead dry, it should all be coated with paraffin except at the lower end. Before using it each time, the carbon should be washed with dilute hydrochloric acid.

There are certain inaccuracies inherent in the results obtained with both of the electrodes described above due to the difference in temperature between the brine and the metal at the point contact is made. However, this error is only a very small per cent of the total potential difference and therefore for this type of work may safely be neglected.

Application of the Protecting System

The essential parts of the cathodic protecting system consist simply of a source of low-voltage, direct current—usally a dry-type rectifier, anode of suitable metal such as zinc or aluminum, resistors, meters and suitable connectors to the cans and pipes to be protected. A wiring diagram of a typical system is shown in Figure 3.

If both cans and ammonia pipes are to be protected, it may be necessary to place separate resistors in series with the ammonia pipes or coils, also as shown in Figure 3, in order to control the current distribution between cans and pipes because, in general, less current is required to protect them than is necessary for the cans.

Once the average temperature of the brine is known, the current density in milliamperes per square foot of can surface may be determined from the curves of Figure 9 or for the ammonia pipes from Figure 10. It can be seen that usually this is around 4 or 5 milliamperes per square foot. Knowing the number of cans and amount of ammonia pipe surface in the plant, the total current needed may quickly be calculated. After the system has been in operation for a short time, the characteristic, gray, protecting film can be expected to appear on the surface of the parts connected. As soon as this film becomes well formed, the current density may be reduced, in the interests of economy, to a value just sufficient to maintain it at all points and at all times.

The ammeter shown in Figure 6 indicates the amount of current going into the system. It should be of a recording type. In order to determine the

amount of electrical energy used, an ordinary watt-hour meter should be installed in the line from the alternating-current source.

Since plant conditions vary so widely, no single set of operating instructions can be drawn up to fit all cases. However, once the system is placed in operation, the test of its effectiveness is in the formulation of the protecting surface film and the absence of corrosion. These conditions can readily be observed by the operators.

Economics of Protection

No method of protection is economically sound unless the real savings are in excess of the cost of protection. Usually it is best to compare these on the basis of annual costs. In addition, there are likely to be other intangible benefits that in the opinion of the operators may outweigh the actual monetary savings.

In protecting ice plant equipment, the expense involved is in the cost of the electrical energy consumed annually as well as in the cost of the zinc anode. Also, it is necessary to include the annual investment charges incident to the purchase and installation of the protecting system. It may be advisable to include a small operating charge needed to keep the system working. The sum of these expenses represents the total annual cost of protection.

Against the above expenses are to be balanced the savings resulting from increased life of the equipment as well as the saving in output, time, and annoyance that otherwise would be caused by the failure and necessary replacement of cans, piping, pumps or even tank.

For any given plant these items undoubtedly vary considerably and all that can be given here is a typical example showing the method of calculating and comparing the cost of protection with the savings resulting from protection. The comparison will be made as for a 400-can plant and for protecting the cans only.

Assuming a brine temperature of 16 degrees F., 3.0 milliamperes per square foot of can surface would be required for a 200-millivolt protecting voltage. See Figure 9. A 300-lb. can has approximately 22 square feet of surface so that a total of 22 x 0.003 x 400 or 26.4 amperes would be needed for all the cans. This current is supplied at a relatively low voltage, in general, only a little more than enough to take care of the voltage drop in the leads from the direct-current source to cans. If fairly large leads are used, this would be on the order of 1.0 volt. On this basis, the energy required would be 1 x 26.4 or 26.4 watt hours every hour. For the 8760 hours in a year, this would then amount to around 231,250 watt hours or approximately 231 kilowatt hours.

Rectifiers have an average efficiency of around 30 per cent, therefore, the alternating-current input would be approximately 770 kilowatt hours and at a rate of 2c per kilowatt hour, this would cost \$15.40 per year or nearly 4c per can per year. To this must be added an investment charge to cover interest, depreciation, taxes and insurance on the installation. A reasonable

figure for this is 10 per cent for interest, taxes, and insurance, and an amount for depreciation depending upon the life of the equipment. For example, equipment that lasts 20 years depreciates 5 per cent per year or if it lasts 10 years it depreciates 10 per cent per year. In normal usage most electrical equipment has a life of 20 years so that a depreciation of 5 per cent is sufficient. This means that the total investment cost of such equipment is 15 per cent of its installed cost.

The cost of the rectifier, wiring connections to the alternating-current source and connections to the ice cans will vary widely from plant to plant and only an estimate by an electrician will show what they really will be. The following figures are not estimates, but are given only as examples. A rectifier to furnish 30 amperes might cost around \$100, switches and connections possibly \$75, and wiring and conduit \$75. Based on labor at \$50, the total would amount to \$300 and of this 15 per cent or \$45 then represents the annual investment cost.

Anode material must be included as an operating expense. One ampere of current will decompose approximately 15.5 pounds of zinc in one year. Therefore, 26.4 amperes will use up 26.4 x 15.5 or 410 pounds. Under normal conditions, this costs around 6 cents per pound, making the total cost for zinc 410 x \$0.06 or \$24.60. An annual operating labor cost of some \$25 completes the total annual cost summarized as follows:

Energy Cost	\$ 15.40			
Investment Cost	45.00			
Zinc anode	24.60			
Operating expense	25.00			
Total	\$ 110.00	for	400	cans
or 27 1/2 cents per can per year.				

Most important on the side of savings is the increased length of life of the cans. Based on a cost of \$10 each, the 400 cans in the plant would cost \$4,000. Without protection, the life of cans may not average over 8 years. On this basis, the depreciation would be 12 1/2 per cent. This added to 10 per cent for interest, taxes and insurance would make a total investment cost of 22 1/2 per cent of \$4,000, or \$900.

With protection a normal life of 20 years may easily be expected. This means 5 per cent for depreciation or a total of 15 per cent for the investment cost which then becomes \$600. The difference between \$900 and \$600 represents the minimum saving brought about by cathodic protection. Probably to this should be added at least as much more to cover the saving in time, ice and annoyance due to frequent failure of unprotected cans. This saving is realized at a cost of \$110 per year. The actual accounting records of the plant will give experience figures to use in place of the above examples.

XII. SUMMARY OF RECOMMENDATIONS ON ICE PLANT CORROSION CONTROL BY CATHODIC PROTECTION

A. Cathodic Protection Procedure

- 1. Determine brine-tank potentials
- 2. Install cathodic protecting system
- 3. Maintain current at correct value
- 4. Inspect cans and piping for protecting film and absence of corrosion
- 5. Start system of records of can replacements and repairs due to corrosion

B. Critical Points in Ice Plant Brine Tanks and Precautions

- 1. Brine line on ice cans
- 2. Seams in ice cans, rivets
- 3. Bottom of ice can-account of entrapped air
- 4. Joints and fittings of ammonia piping
- 5. Brine agitator propellors

C. Precautionary Aids in Reducing Corrosion

- 1. Use chemical treatment also
- 2. Keep a variety of metals out of tank
- 3. Buy cans with welded seams and openings into space beneath bottom
- 4. Avoid brass air pipes welded to side of can
- 5. Avoid brass in contact with steel anywhere

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