

# Gas Appliance Engineers Handbook

## SECTION 1 - FUNDAMENTALS

### CORROSION

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#### INTRODUCTION

The subject of corrosion is very broad and complex. Its ramifications cover many fields of theory, fact and methods for corrosion control. There are many textbooks, handbooks and volumes of technical publications on corrosion that date back as early as 1824 when Sir Humphrey Davy published his studies.

No attempt therefore will be made to cover the overall problems and emphasis will be made only on those phases which are thought to be of general interest to the gas appliance engineer with particular emphasis on the ferrous metals. References will be made wherever possible so that those who are interested may investigate and study the subject at greater length.

The corrosion of common every day metals and metallic alloys is affected by many variables which may or may not be mentioned herein. It is suggested that answers to any specific corrosion problem may be found by closely checking the appropriate reference, at the end of the paper.

#### WHAT IS CORROSION?

"Corrosion of a metal is the destruction of the metal by its environment through chemical or electro-chemical means". Every known metal is subject to corrosion. Some metals corrode faster than others; some so fast that they are a definite fire hazard, others so slowly that their corrosion cannot be seen by the naked eye. The corrosion rate of every common metal is known and no two rates are exactly the same. The corrosion of metals depends upon many factors.

Most metals do not appear in nature in their pure form and are generally found in compounds united with other elements. The minerals found in the earth and rocks and in the salts of the sea are stable combinations of compounds such as oxides, sulfates, chlorides, phosphates, etc. Ever since man through his

own intelligence contrived to reduce various metallic compounds to useful engineering materials, he has been constantly confronted and challenged by the fundamental laws of nature that, through the process of corrosion, a refined metal will "drive" toward achieving its native stable state.

The wastage of metals by corrosion usually makes itself evident by the presence of a corrosion product such as rust on iron (1). When you analyze rust you find it is iron oxide. When you analyze natural iron ore, you also find that it too is iron oxide. In the corrosion of purified iron it has reverted to its original native state, iron oxide.

Different metals are affected to different degrees and corrosive attack may take many different forms. Attack may be by general tarnishing or rusting (2).

1. Corrosion may develop near or at the junction of two dissimilar metals (3).
2. The metal may suffer highly localized attack by pitting (4).
3. The strength of a metal may be destroyed by cracking induced by corrosion (5).
4. Corrosion may also be confined to crevices, under gaskets or washers, or in sockets (6).
5. It may have the effect of removing one of the constituents of any alloy so as to leave a weak residue (7).

Thus the forces that cause corrosion are constantly at work. It costs billions of dollars a year. It dissipates our resources and the fruits of our labor. It interrupts production. It causes accidents (11). "This is corrosion".

#### THEORY OF CORROSION

The theory of widest applicability and acceptance is the electro-chemical theory of corrosion. By definition, electro chemistry is the science of the relation of electricity to chemical changes. "When a metal is in

# Gas Appliance Engineers Handbook

contact with water, there is a tendency for the atoms of the metal to become ions and go into solution, leaving their electrons on the metal, thus giving the metal a negative charge" (Nernst Theory).

The subject of corrosion is electro-chemical and the rate of corrosion is simply a function of electromotive force and resistance of circuit (8). There is almost always a flow of electricity between certain areas of a metal surface through a solution capable of conducting an electric current (9). This electro-chemical action causes destructive alteration or eating away of a metal at areas which are called anodes where the electric current leaves the metal and enters the solution.

Thus the solution or the electrolyte may be considered as one of the main requisites for the progress of corrosion. This can be the moisture in the air or a solution completely immersing the metal and must contain ions. Ions are electrically charged atoms, or groups of atoms, in solution. Pure water, for example, contains positively charged hydrogen ions and negatively charged hydroxyl ions in equal concentration. So the electrolyte may be any form of moisture or solutions of acid and alkali. In the mechanism of corrosion there is always an electrolyte that contains many ions, an anode and a cathode. The anode and cathode may be two dissimilar metals, or may be different areas on the same piece of metal. In either case, there must be a potential difference between the anode and the cathode, so that electricity will flow between them. The electrical circuit is completed by a metallic path which permits the negative charged electrons to move from the negative to the positive.

For example, a piece of iron is put into

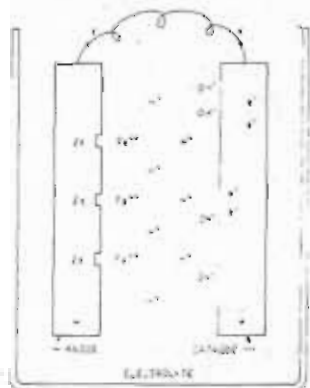
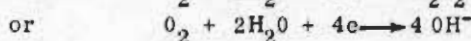
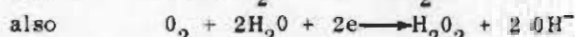
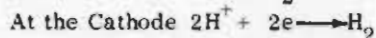


Figure 1

the same electrolyte with a piece of copper. The iron will become the anode and the copper the cathode. Positively charged atoms of iron will pop-off the iron surface and enter the electrolyte as ions. Two corresponding negatively charged electrons per iron ion will be left behind on the iron. The electrons will then flow to the cathode by means of the metallic bridge between the two. Figure 1.

## Chemical Reactions (10)



When the electrons reach the cathode with their negative charge, they will attract the positively charged hydrogen ions in solution and will neutralize some hydrogen ions. In losing their charge, the positive ions become neutral atoms and combine to form hydrogen gas. Thus, there is usually hydrogen gas liberated at the cathode during the corrosion process.

Some of the hydrogen ions thus released will unite with oxygen ions in solution and will form hydroxyl ions ( $OH^-$ ) which tend to cling to the cathode. These hydroxyl ions will make the solution at the cathode less acid and consequently less corrosive.

To summarize this corrosion process there must be:

1. A release of electrons at the anode;
2. Formation of metal ions through disintegration of the anode;
3. Flow of the electrons to and accepted by the cathode;
4. Neutralization of the positive ions or formation of new negative ions.

Action at either the anode or cathode cannot go on alone. The two reactions go on at the same time at equivalent rates and corrosion occurs at the point where the metal ions enter into the electrolyte.

This corrosion process does not necessarily have to be between two dissimilar metals but can occur on the surface of a single metal. There will be many local areas on a piece of metal that will be either anodic or cathodic and the same procedure will take place between these dissimilar areas. If there

is an electrical potential difference between two areas and these areas are in contact with the same electrolyte, then corrosion can occur.

The flow of electric current is a result of or a product of corrosion and if this current can be measured, the degree of corrosion can be estimated.

## GALVANIC CORROSION

When two dissimilar metals are in contact with one another or otherwise electrically connected and exposed to the same corrosive liquid, a potential is set up between these two metals and an electric current flows. This is called "Galvanic Corrosion". This phenomenon can cause excessive corrosion or in some cases can be put to useful work as in an electric battery. The storage battery uses this principle where two dissimilar metals are immersed in a strong electrolyte under ideal conditions for producing a relatively strong electric current.

In the bi-metallic cell thus formed another phenomenon takes place. One metal (anode) corrodes much faster than it would under normal conditions and the electric current thus generated will flow to the more noble metal (cathode) and this current will decrease

the corrosion of the cathode as long as the anode is present and active. This is in many cases an unfortunate situation in that the weak link in the chain becomes weaker. Or one metal may be sacrificed or expanded to save the other.

In general it is possible to determine from their respective positions in the Electromotive Force Series, which of the metals will corrode the fastest. (Table 1). Hydrogen gas has been used as an arbitrary reference element.

Those elements above hydrogen in the list become progressively more active and those below hydrogen progressively less active. One extreme is potassium which reacts so violently in moist air or water that it will burst into flame. The other extreme is gold and platinum which corrode very slowly.

This series will show which metal will displace another and suffer accelerated corrosion in the process. Any metal will displace one below it. For example, iron will displace tin in solution. If there are tin ions in the electrolyte they will be plated out on the iron, thus giving it a coating of tin. This process is used commercially in metal plating. However, if the iron and tin are placed in the same electrolyte and are electrically connected then the iron will go into solution and will corrode instead of the tin.

The series also gives an indication of the potential that should exist when two metals are connected together. The farther apart the metals are in the series, the greater the potential and the greater the likelihood of galvanic action. For example, magnesium and copper form a bad combination, since galvanic action would most likely occur with the corrosion of magnesium greatly accelerated. Conversely, there would be little action between lead and tin.

Galvanic corrosion is readily recognized by mere visual examination. The accelerated corrosion of the less noble metal is usually localized near the point of contact and often manifests itself as pits, grooves and channels.

The rate of galvanic corrosion depends in part upon the potential difference between the two metals. This difference can be measured in millivolts and depending upon the strength of the electrolyte will increase with a change of several factors such as temperature, oxygen solubility, etc. If the two metals are put into metal contact then the degree or rate of corrosion can be measured in milliamperes.

### Galvanic Series of Metals & Alloys

Electromotive Series		Practical Series. Material
Metal	Volts	
Magnesium **	-1.55	Magnesium*
Aluminum ***	-1.33	Zinc
Zinc **	-0.76	Aluminum 2S
Chromium **	-0.56	Cadmium
Iron **	-0.44	Steel or iron
Cadmium **	-0.40	Cast iron
Cobalt **	-0.29	Iron, 13% Cr (active)
Nickel **	-0.23	Ni-Resist
		18-8S (active)
		18-8S Mo (active)
		Chlorimet 3
		Hastelloy C
		Lead
		Nickel (active)
		Inconel (active)
		Hastelloy A
		Chlorimet 2
		Hastelloy B
		Brasses
		Copper
		Bronzes
		Copper-nickel alloys
		Monel
		Nickel (passive)
		Inconel (passive)
		Chromium iron (passive)
		18-8S (passive)
		18-8S Mo (passive)
		Silver
		Gold
		Platinum <sup>b</sup>
Antimony ***	+0.1	
Copper **	+0.34	
Silver **	+0.8	
Gold ***	+1.36	

\* Corroded end (anodic or least noble).  
<sup>b</sup> Protected end (cathodic or most noble).

Table 1

# Gas Appliance Engineers Handbook

Thus, the potential between two dissimilar metals is measured in millivolts and the rate of current flow between the two is measured in milliamperes. (See Table II).

## Effect of Temperature on Electrical Current Flow Between Dissimilar Metals in Cleveland Tap Water

Temp. °F	Current (Milliamperes)			
	Copper Galv. Iron	Brass- Galv. Iron	Brass- Iron	Brass- Copper
70	1.49	1.13	.45	.08
80	1.68	1.34	.53	.08
90	1.87	1.60	.62	.09
100	2.12	1.94	.74	.10
110	2.50	2.30	.86	.11
120	2.82	2.60	.97	.12
130	3.14	2.91	1.14	.13
140	3.36	3.09	1.39	.14
150	3.53	3.26	1.79	.15
160	3.64	3.43	2.34	.16
170	3.67	3.55	2.74	.17
180	3.59	3.62	2.95	.17
190	3.43	3.70	3.08	.18

TABLE II.

Change in temperature will also affect the extent of current flow. Some cases have been observed where an increase in temperature has actually reversed the direction of current flow between two metals, so that at one temperature metal "A" would suffer galvanic attack, while at a higher temperature "B" would be the one affected.

As corrosion progresses both types of current may decrease. This is due to the generation of corrosion products at both the anode and the cathode. The generation of hydrogen at the cathode will tend to put a protective film over the cathode thus reducing the potential between the two metals. Or, this hydrogen gas may react with the oxygen in the solution to form a hydroxyl ion which being alkaline will also reduce the potential. Consequently, this potential will vary with circumstances and will not be a constant factor. When these by-products of corrosion build up they will tend to polarize the electrodes decreasing the potential. Some metals will polarize more quickly or readily than others.

This polarization however can be depolarized just as easily by the removal of the protective film. The hydrogen film for instance can be removed by excess oxygen in

the solution or it can be washed off by agitation of the solution thus permitting corrosion to continue.

The change of potential is also affected by the current density. "Current density is that current per unit area of exposed surface and is expressed in milliamperes per square foot".

For example, for the same amount of current the current density on a large cathode will be less than on a small one. Thus the hydrogen developed will be spread out more thinly and will be more easily depolarized.

The designing engineer should eliminate wherever possible the direct contact of dissimilar metals. If this is not possible then certain precautions should be taken, otherwise severe galvanic corrosion of one or more of the parts may occur.

1. The area of a more anodic metal should be larger than the area of the cathode. If this is not done, the corrosion rate on the anode may be quite severe.
2. Dissimilar metals in contact with the same electrolyte should be electrically insulated.
3. Paint both anode and cathode. Do not paint or cover one without doing the same to the other and keep in good repair.
4. Galvanic current can be greatly reduced by the addition of certain inhibitors (6).

### STRAY CURRENT CORROSION

This form of corrosion designates the damage caused by electric currents other than the intended circuit or by impressed extraneous currents.

Stray current corrosion occurs most often in moist soils and is characterized by severe local pitting at the point where the current leaves the structure. Structures most commonly affected are buried pipe lines and the like.

The offending or stray currents are usually those which leak from electric power circuits and flow through the earth and through metallic structures buried therein. Return circuits of electric railways, electrified systems and plants using direct-current constitute the chief source of stray currents. Fortunately, those current leaks are easily recognizable and today major corrections and preventative methods are used to prevent

such occurrences. Complete insulation of the possible generating sources is recommended although these are not wholly effective in all instances. (6), (7).

## WATER COMPOSITION

The corrosion of a metal by water is an electro-chemical process; chemical in that the metal is converted to a compound; electrical in that the flow of an electrical current (self-induced or imposed) is associated with that conversion.

In tracing the flow of a corrosion current two pathways are clearly in evidence. One is the metal itself through which free electrons flow from areas of high potential (anodic areas) to areas of low potential (cathodic areas). The second pathway is through the electrolyte: water, wet soil, salt solution, acid solution or other suitable liquid medium through which ions migrate freely between the anodic and cathodic areas of the affected metal. Both paths together constitute the circuit of the corrosion current, while the electrolyte in combination with the anodic and cathodic areas of the corroding metal form the corrosion cells.

The electrolyte is the corrosive medium which surrounds and touches the surface of the metal. In the case of water heaters it is the hot water in the storage tank. Free electrons do not move through the electrolyte; they are taken up by the positive ions ('cations) at the cathode and given up by the negative ions (anions) at the anode. The electrical current is thus ferried across the electrolyte by the ions.

The corrosion rate of a ferrous metal is controlled not by the readiness with which electrons flow through the metallic path but rather by the chemical character of the water itself, (the electrolyte). Any alteration in the chemical characteristics of the water, or in the ease with which water reacts with the metal, or in the frequency with which certain constituents of the water pass over a given spot on the metal will influence the corrosion rate.

That property which renders a water aggressive to metals is termed its corrosivity. The active agents contributing to the corrosivity of water, aside from the solvent action of the water itself are: acids; salts, which yield acids by hydrolysis; dissolved oxygen;

carbon dioxide; hydrogen sulfide; ammonia; chlorine; other aggressives.

All natural waters contain dissolved mineral matter. Water in contact with soils and rocks, even for a few hours, will dissolve some mineral matter. The chemical identity, character and quantity of mineral matter contained in a natural water depend primarily on the type of rocks and soil with which the water had come in contact, and how long it remained in contact. Some streams are fed by both surface runoff and groundwater from springs and seeps. Such streams reflect the chemical character of the more concentrated ground water during dry periods. In periods during heavy surface runoff, however, these streams are more dilute. Ground water usually contains more dissolved mineral matter than surface runoff for it remains in contact with soils and rocks for longer periods of time. The concentration of dissolved solids in a river water may be increased by drainage from mines and oil fields, by discharge of industrial and municipal wastes into the streams and in irrigation areas by return drain waters.

Marked variations in the characteristics of waters utilized in domestic water heaters prevail on a nationwide scale. By way of illustration, dissolved solids alone may range from as little as 10-20 parts per million in some New England waters to as much as 3000-6000 parts per million in some of the highly mineralized waters of the Southwest. Similar examples of variability can be cited with respect to pH, hardness and corrosivity.

Among the dissolved solids and gases commonly reported in a water analysis are:

- Aluminum; Manganese and Iron;
- Calcium and Magnesium;
- Sodium and Potassium;
- Oxygen and Carbon Dioxide;
- Carbonate and Bicarbonate;
- Sulfate, Chloride, Fluoride and Ammonia.

In addition, it is customary to report the total dissolved solids, specific conductance, pH, and total hardness.

The total dissolved solids indicate the total weight of dissolved mineral matter in the water, usually expressed as parts per million. By itself, this value gives no indication as to the identity of the mineral matter or the corrosivity of the water.

The specific conductance of the water is a measure of its capacity to conduct an electric



# Gas Appliance Engineers Handbook

current. Since the corrosion process involves in part the flow of an electric current, the specific conductivity indicates the readiness with which a corrosion current can flow through the electrolyte. In addition it furnishes a rough measure of the mineral constituents of the water, although it gives no indication of the relative quantities contained in the solution.

The pH is a measure of the acidity or alkalinity of the water. A pH of 7 is regarded as neutral; above 7 alkali; below 7 acid. Because of the relation of pH to corrosivity, many waters are chemically treated to adjust the pH to reduce corrosion in distribution systems and household installations.

Hard Waters: Hardness in water is objectionable for its soap destroying and scale-forming properties, and will vary considerably in different sections of the country. Since hardness is caused primarily by calcium and magnesium ions, sections having limestone formations almost invariably have a higher hardness content than open streams in the same section because the open streams contain larger quantities of rain water which have not come in as intimate a contact with the mineral formations of the earth.

Hardness, which is chemically expressed as parts per million calcium carbonate (ppm  $\text{CaCO}_3$ ) is customarily reported as:

1. Carbonate hardness -- ppm  $\text{CaCO}_3$
2. Non-carbonate hardness--ppm  $\text{CaCO}_3$
3. Total Hardness--ppm  $\text{CaCO}_3$

Carbonate hardness is that due to calcium and magnesium bicarbonate and carbonate, while the non-carbonate hardness is due to calcium and magnesium sulfates, chlorides, nitrates. Carbonate hardness is sometimes referred to as temporary hardness (removed by boiling) while the non-carbonate hardness is sometimes referred to permanent hardness (cannot be removed by boiling). Total hardness is the sum of both.

In terms of hardness, natural waters may be generally classified as follows:

<u>Hardness</u>	<u>Classification</u>
Less than 15 ppm	Very soft water
15 to 50 ppm	Soft water
50 to 200 ppm	Medium hard water
100 to 200 ppm	Hard water
Greater than 200 ppm	Very hard water

The corrosivity of waters, which varies from one supply to another is determined not by the degree of hardness alone, but rather

by a combination of factors derived from a chemical analysis. Especially important are:

1. Free oxygen and carbon dioxide
2. Total hardness
3. Methyl orange alkalinity (alkalinity due to bicarbonate and carbonate)
4. Chloride radical
5. Sulfate radical
6. pH

The fact that the chemical composition of water influences corrosion rates has been recognized for a long time and much effort has been devoted to classifying waters as corrosive and non-corrosive on the basis of their composition. Considerable emphasis, however, has been placed on the Langelier Index -- a numerical term which is equal to the difference between the measured pH of a given water and the pH of the same water saturated with calcium carbonate ( $\text{CaCO}_3$ ). This index is also known as the Saturation Index.

If the measured pH is greater than the pH at saturation it indicates that the water is supersaturated with calcium carbonate and that the water is generally considered non-corrosive. Such water is said to have a positive Langelier or Saturation Index. If, however, the pH at saturation exceeds the measured pH, the water is said to have a negative Langelier Index and is usually considered corrosive.

Waters with a positive saturation index tend to deposit protective films of calcium carbonate on metals. To a large extent, it appears as if the film provides protection by forming a barrier to the oxygen diffusing to the metal. Although useful as an approximate guide, the Langelier Index is not proportionate to the velocity of the corrosion reaction, and therefore cannot be used to predict the length of time a metal will last before corrosion failure occurs.

Rated by aggressiveness, water supplies may be conveniently grouped as follows:

1. Relatively non-aggressive (protective)
2. Moderately corrosive
3. Strongly corrosive because of high salinity
4. Strongly corrosive because of high  $\text{CO}_2$ ,  $\text{O}_2$ , and low carbonate.

The essential characteristics of Group 1 are a very high carbonate hardness, relatively low salinity, an alkaline pH value, and a low oxygen and carbon dioxide content. The non-

aggressive (protective) character of this group is due largely to the high carbonate hardness. The carbonates which are precipitated from the decomposed bicarbonates in the hot vessel or pipe form an adherent, bulky deposit which prevents direct contact of the water with the metal surface, hindering any appreciable corrosive action.

The second group (moderately corrosive waters) is characterized in general by a medium carbonate hardness, relatively low salinity, an almost neutral pH and a low free carbon dioxide content. The lower carbonate hardness in this group distinguishes it essentially from Group 1. The tendency to precipitate lime is much smaller in this group. In the absence of this protective effect, the salinity, though low, tends toward moderate corrosion. Such free CO<sub>2</sub> that may be present enhances the corrosive tendencies.

The strongly corrosive waters of Group 3 are characterized by their high salinity. These usually contain free mineral acids, low carbonate hardness, a high sulfate content and an acid pH value.

The strongly corrosive waters in Group 4 are characterized by a high free carbon dioxide content and low carbonate hardness, low salinity and acid pH value.

Water composition is an important factor in corrosion rates of metals. Waters that do not form scales and which are high in dissolved oxygen and free carbon dioxide are more corrosive than those which do form scales and are low in these dissolved gases.

In a test conducted at the Case Institute of Technology, Cleveland, Ohio, by The American Gas Association on a series of unprotected galvanized storage heaters, two test waters were used: (1) Cleveland tap water, unsoftened; (2) Cleveland tap water, Zeolite-softened. Chemical analysis showed that by passing Cleveland tap water through gel-type water softener there was no change in the dissolved oxygen nor in the free carbon dioxide content. However the scale-forming character of the water was changed by the removal of calcium and magnesium and their replacement by sodium. While the total dissolved solids and the total oxygen and carbon dioxide remained virtually unchanged, the waters differed as expected in scale-forming properties.

The data presented in Figure 2 show there was more corrosion in those heaters utilizing

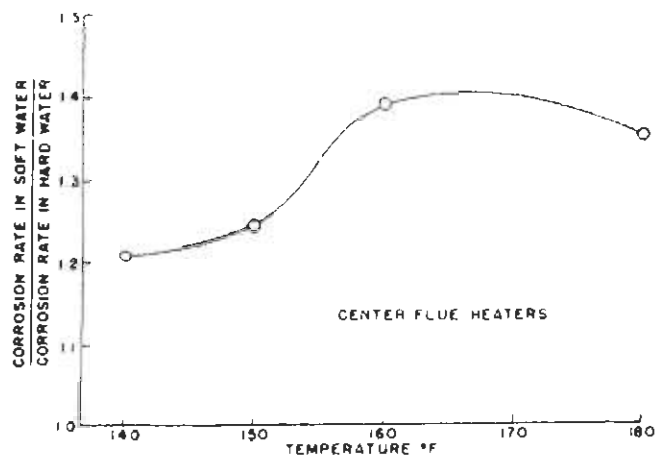


Figure 2 - Relative Corrosion Rates of 30-Gallon Center-Flue Heaters by Zeolite-softened Water Compared to Rates by Unsoftened Water.

Zeolite-softened water than those heaters utilizing the unsoftened water. In this comparison it is shown that in Zeolite-softened water the corrosion rate is 1.22 times greater at 140° F., 1.25 times greater at 150° F., 1.39 times greater at 160° F., and 1.36 times greater at 180° F. than in unsoftened water at corresponding temperatures.

## CATHODIC PROTECTION

Corrosion may be suppressed by changing the characteristics of the metal or its environment. One of the most widely accepted methods for altering the corrosion character is to force a small direct electric current onto the metal. This is the reverse aspect of galvanic corrosion. So, what was previously the anode is now reversed and becomes the cathode. Or, a physical means of counteracting galvanic corrosion where the electrochemical force is reversed with the subsequent stoppage or retardation of the destructive process is called "Cathodic Protection".

Direct current from any source, properly applied in a sufficient quantity to all parts of the metal, will stop the corrosion of the metal. This fact has been used for many years. In some cases this direct current has been generated by the battery action of dissimilar metals. In other instances the direct current is supplied by electric batteries, generator sets or by converting conventional alternating current.

The principle of cathodic protection was used as early as 1824 when Sir Humphrey

# Gas Appliance Engineers Handbook

Davy used zinc anodes in sea water to protect the copper plates of seagoing ships. However, this led to another problem. The toxic effect of corroding copper previously helped to prevent fouling by marine organisms. Thus the elimination of one problem may often times create another problem and the corrosion engineer again should be cognizant of the various factors involved.

When compared with other methods of corrosion control, properly understood and properly applied, cathodic protection has many advantages. In most cases it is easily applied with a minimum of labor without the disassembling of structures and equipment.

## GALVANIC ANODES

A common and economical method for producing this protective current is the use of Galvanic Anodes such as magnesium, zinc and aluminum. These less noble metals will, when submerged in certain electrolytes, generate a relative degree of direct current. For example, zinc has a normal difference in potential from that of steel of 0.32 V., while aluminum and magnesium have differences of 0.89 and 1.11 V. respectively. Obviously, magnesium offers the best choice to generate a higher voltage. Magnesium alloy anodes have been used with much success to retard corrosion of steel. Properly installed they will prevent corrosion of hot water storage tanks, water carrying vessels, buried steel structures and pipe, ship hulls, oil tanks, etc. (15), (16).

To be effective the anode must provide a continuous flow of current which must not be restricted by any tendency to form a self-protection scale (17). Basically, when the applied current density is sufficient to eliminate the potential difference between the local anodes and local cathodes, protection is obtained.

## SHEATHED ANODES

Where sacrificial anodes, such as magnesium, are used for cathodic protection the life of the anode is a variable of great degree. The variables which will greatly affect the anode life are anode purity, temperature, strength of the electrolyte and the potential difference between the anode and the cathode. The current flow from the

anode is greatly affected by the electrical conductivity of the electrolyte (dissolved solids).

Generally, an anode will deliver considerable more protective current than is required. Such a waste of current will reduce the effective life of the anode. If this current could be regulated to that actually required for adequate protection without excess current being produced, the life of the anode will be greatly increased.

Resistors in the electric circuit have been used with a degree of success, however at a sacrifice of anode efficiency. When electrical resistors are used and when electrical resistance is built-in in the cathode itself, such as with porcelain enamel, the current efficiency of the anode is greatly reduced (13).

Increased magnesium efficiency has been obtained by "sheathing" the anode with various materials such as aluminum metal, plastics, rubber, ceramics, etc. Holes are punched in the sheath and these are so spaced that only a small area of the bare metal is exposed to the corrosive electrolyte.

Tests made on glass-lined hot water tanks under normal corrosion attack indicated that with anode covering of 85 to 95 percent, the protective current generated was as much as that produced by a bare anode. Thus the current density of the anode is greatly increased with resulting higher anode efficiency which should also result in longer anode life (13), (16).

## POWERED ANODES

The corrosion character of a metal may be altered by impressing on it a small direct current. This may be accomplished in more ways than one. Direct current from any source, properly applied and in sufficient quantity to all parts of the metal, will stop the corrosion of that metal.

This electric current may be supplied with sacrificial anodes, such as magnesium, or the current may be supplied directly by means of an electrode. When electrodes are used for cathodic protection they are usually non-sacrificial or permanent anodes such as platinum, graphite, high silicon iron alloys and platinum coated tantalum. The electric potential of each of these is such that a direct electric current is not spontaneously generated to flow from the



# Gas Appliance Engineers Handbook

anode to the cathode. The current must be forced from the anode onto the cathode.

Materials from which the current must be forced in order to provide protection, are called Powered Anodes. Any source of direct current of sufficiently high voltage and current capacity will suffice to operate a powered anode. Examples of such sources of electric energy are, thermo-electric generators, solar batteries and rectified alternating current.

Although the type of protective electric current produced by a sacrificial magnesium anode is identical to that flowing from a powered anode fabricated from an inert metal, there is a difference in the chemical reactions which occur at the anode. In the case of magnesium anodes there is no oxygen produced, whereas there is oxygen produced by powered anodes if these latter are of the permanent type. Thus, use of powered anodes can result in a mixture of oxygen and hydrogen gas (12).

The volume of gas produced may be calculated from Faraday's "Laws of Electrolysis". The volumes of hydrogen and oxygen, as well as the sum of these two volumes are a function of the quantity of protective current generated.

Powered anodes have chiefly been used for protection to large structures such as water stand-pipes, buried pipe lines, bridges and the like. The cost of the generating equipment is generally proportional to the amount of current required for protection. This cost may vary from many thousands of dollars for a large structure to a couple of dollars required for protecting a 30-gallon hot water storage tank.

## CORROSION FROM FLUE GASES

Gas burning appliances and flue ways may be subjected to severe corrosion problems from the mere fact that combustion products aggravate normal corrosion. When gas burns with complete combustion the by-products of this combustion are water vapor and carbon dioxide, both of which tend to promote corrosion. Add to these temperature, sulphur, excess oxygen and condensates, and you have a combination of many variables.

There is considerable information available on these various factors. Probably the most appropriate information to the gas appliance engineer are the corrosion studies

made by Battelle Memorial Institute for the American Gas Association, Project DGR-4-CH. Such factors as:

- (a) Sulphur content of fuel gases;
- (b) Temperature and time;
- (c) Condensation and re-evaporation;
- (d) Other influencing factors;

were studied with corresponding results. Also a very comprehensive study on the corrosion behavior of metals in condensing flue gases has been carried out by Shnidman (18).

Vapor sulphur in the presence of moisture and condensates has a very serious corrosive effect on many steels. Aluminized steel has remarkable ability to withstand this type of attack in most appliances. Operation of appliances in which some parts or sections of the equipment would reach temperatures above 800° F. is also a serious problem. Areas where moisture and condensates can collect even for only short periods of time, should be eliminated wherever possible.

## HIGH TEMPERATURE CORROSION

The corrosion of steel and various steel alloys at elevated temperatures is a complete study in itself. Basically, steel alloyed with nickel or chromium or both have greater resistance to corrosion than plain carbon steel. Resistance to oxidation and erosion are important but consideration must also be given to other factors such as tensile strength, impact strength, temperature embrittlement, etc. (19).

Local cold working of the metal may leave it in a strained condition causing accelerated corrosion. Polished surfaces generally are less subject to corrosion than rough surfaces. The presence of mill scale on the surface forms centers of corrosion.

At high temperatures, chromium steels are oxidized less than are carbon steels and form a characteristic colored tempering film as illustrated in Table 3 (20). Pilling and Bedworth (21) after a careful study of oxidation of metals, conclude that it is a diffusion process dependent mainly upon the physical properties of the oxides produced.

There is no simple or valid rule for the prevention of scaling except that of discovering and applying a coating which is protective and semi-permanent under the particular

# Gas Appliance Engineers Handbook

operating conditions. Considerable development of special steels, protective coatings and inhibitors have been made in the last few years and it is recommended that the engineer take full advantage of the latest information which is generally available from the material suppliers.

ment of corrosion. Laboratory, accelerated bench and beaker tests may give considerable valuable information to the corrosion engineer. However, one should be cautious of making conclusions based upon such tests since they may be only indicative and not represent the complete and true answer to

Table 3: Tempering Colors

Color	Appears on Carbon Steel		Appears on Stainless Steel	
	Deg. C.	Deg. F.	Deg. C.	Deg. F.
Pale straw	220	420	250	482
Dark straw	230	446	300	572
Dark straw-brownish	240	464	350	662
Brownish-purple	260	500	400	752
Reddish-purple	270	518	450	842
Full purple	290	554	500	932
Blue purple	300	572	550	1022
Dark blue	310	590	600	1112
Greenish blue	320	608	650	1202
Steel gray	340	644	700	1292
Brownish gray	360	680	750	1382

Stainless Steel containing 13% chromium and 0.3% carbon compared with high carbon steel.

## CORROSION PREVENTION

When the engineer understands the theory of corrosion and the conditions that cause corrosion, then and only then can corrosion be controlled. Most often the corrosive measure is obvious such as the proper use of the right metal in the correct environment. Quite often all that is necessary is to change the environment. This may be the elimination of moisture or the use of inhibitors to cover the corroding metal with a protective film (14). Even paint may be the practical answer (22).

Most metals can be protected with cathodic protection by using a galvanic or powered anode which will supply an electric current to counteract the natural corrosion currents (15).

Many test methods and procedures have been developed for the checking and measure-

a specific problem. All observations should therefore be regarded as relative. Unfortunately, there are so many variables in the corrosion process that are specific to the particular metal, only time is the true measuring stick. Proof of corrosion results generally lie in long-time procedure and field testing under actual operating conditions where all the variables have a chance to show their effect and counter-effect.

There may not always be a perfect or complete answer to a specific corrosion problem. There are, however, many satisfactory and practical methods whereby corrosion can be eliminated or controlled. Sometimes the answer may be more costly than the metal to be protected. Consequently, it is up to the engineer to dig out the facts and what he understands -- he can control or arrive at a conclusion that is commensurate with the facts.

# Gas Appliance Engineers Handbook

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