

## Fundamentals of Metallic Corrosion in Fresh Water

By J.R. Rossum

In preparation for this paper, I've examined some of the available literature on water well corrosion. I find that much of the material is either wrong, terribly confusing, or else completely misses the point. For example:

*"When water contains less iron than the maximum that it is capable of carrying in solution, it corrodes iron or steel rapidly - unless a protective film or crust of some material covers the metal surface. The unsaturated water tends to dissolve metal from the surface of well screens, well casing or piping systems until it becomes saturated with respect to iron. If the mineral content of the water is such that a protective film is not formed by deposition of insoluble materials, severe corrosion results." [1]*

This concept is true only if we are talking about metallic iron rather than ionized iron. However, the solubility of metallic iron in water is not reported in the literature, and is probably too small to measure. Serious corrosion of steel casing from the solution of metallic iron would take centuries or millenia.

Corrosion experiments have not produced entirely satisfactory results. When a commercially useful metal is immersed in water, we know it's going to corrode. The question is, how fast? Since the useful life of most water facilities is often several decades, some corrosion experiments take too long to be practical. If the rate of corrosion is accelerated, the very thing we want to know has been distorted. While corrosion rates can be studied experimentally, in general these rates change with time.

Corrosion in fresh water very often results in pitting so that, because of statistical variation in pit geometry, experiments under identical conditions will not yield identical results.

The result of changes in experimental conditions may appear to be contradictory. For example, normally an increase in temperature will increase the corrosion rate, but it is possible for an increase in temperature to increase the Lagelier Index to a point where the corrosion rate is greatly reduced.

Because of these inherent difficulties, the results of experiments have failed to yield enough information to enable corrosion engineers to calculate the useful life of pipe or other metallic

facilities exposed to water. Nor is chemical thermodynamics particularly useful, since this subject deals largely with equilibrium conditions. The information presented herein is based upon observation of corroding structures and the application of elementary chemical theory.

In conversations, I have found that well drillers often use the term "corrosion" to mean any process that causes incrustation. I will use the term to express a chemical attack on the metal. Since corrosion products sometimes adhere to the metallic surface, and are more voluminous than the corroded metal, corrosion often causes incrustation. However, there are many instances where incrustation occurs without corrosion.

Corrosion in fresh or salt water is always the result of an electrochemical reaction. To one who is not a chemist, the ten-n "electrochemical reaction" seems to denote a complicated phenomenon. As used to describe the corrosion of metals, the application of electrochemical theory allows one to separate the relatively complicated corrosion reaction into two simple parts: the anode reaction where the metal is oxidized, and the cathode reaction where the oxidizer is reduced. Neither of these reactions will occur without the other. Writing them as separate reactions is done only to describe how the overall corrosion reaction takes place. I hope that, by describing the chemical reactions that occur in a galvanic cell, I can make this clear.

A galvanic cell results when two dissimilar metals are placed in an electrolyte. An electrolyte is a solution that contains ions (atoms or small groups of atoms that carry an electric charge) so that it will conduct electricity. Pure water is a weak electrolyte and is a fair insulator or very poor conductor of electricity. It contains approximately 1/10,000,000 of a gram of hydrogen ions (H<sup>+</sup>)

per liter and 17/10,000,000 of a gram of hydroxyl ions (OH<sup>-</sup>) per liter. Since a hydroxyl ion weighs 17 times as much as a hydrogen ion, the two are chemically equivalent and there is no net charge. Sea water is a strong electrolyte that contains almost 4% common salt that ionizes into sodium ions (Na<sup>+</sup>) and chloride ions (Cl<sup>-</sup>).

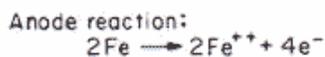
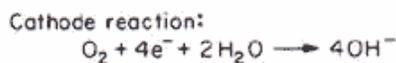
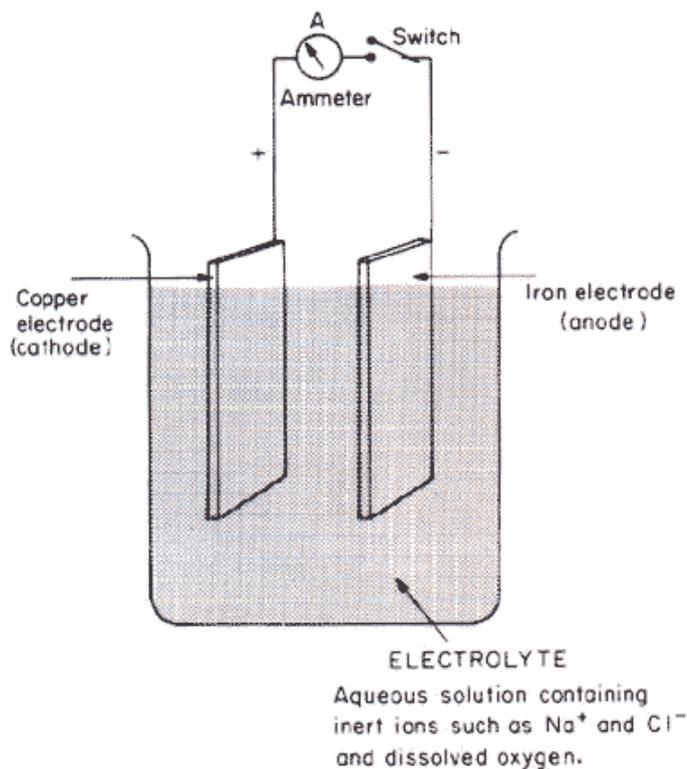


Figure 1 shows a galvanic cell, consisting of two metal plates, one of which is steel and the other copper. As soon as the switch on this galvanic cell is closed, iron starts to corrode.



Neutral iron atoms become ferrous ions with the liberation of two electrons. These two electrons pass through the ammeter to the copper electrode where they react with dissolved oxygen in the water to form hydroxide ions:



FIGURE 1. Galvanic Cell

Electric current flow through an electrolyte is by ionic migration. Positively charged ions ( $\text{Na}^+$ ,  $\text{Ca}^{++}$ , etc.) flow to the cathode (more noble metal) while the negative ions ( $\text{Cl}^-$ ,  $\text{SO}_4^-$ , etc.) flow to the anode. Electron flow through water cannot occur. Since electrons are involved, these corrosive reactions must occur at the metal-electrolyte interface.

When the switch shown in Figure 1 is closed, a short-circuited galvanic cell is created (assuming negligible resistance in the external circuit). Thus the entire voltage drop occurs inside the cell. It can be shown with suitable equipment that most of this voltage drop occurs at the surface of the copper cathode.

The current flow is greatest initially. It decreases rapidly at first, more slowly later on. This decrease is caused by "polarization". Part of polarization results from depletion of the oxygen molecules in the electrolyte immediately adjacent to the cathode surface. The rest of it is caused by some phenomenon for which there is no completely satisfactory explanation. Some authorities attribute this phenomenon to the formation of various films.

I think the easiest way to understand polarization is to look at each cathode material as a catalyst for the reduction of oxygen. It is generally accepted that the reduction of oxygen does not occur directly, and that hydrogen atoms from water plate out on the cathode. It is these hydrogen atoms that react with the oxygen. For the purpose of this discussion, the exact mechanism is immaterial. The net result is that oxygen is reduced, and hydroxyl ions are formed. Those metals that polarize the least (platinum, graphite) are good catalysts. Silver, copper, nickel, and their alloys are fair catalysts, while stainless steel, which has very large polarization, is a poor catalyst. According to this view, oxygen over-voltage is the activation energy for the cathode reaction.

Engineers are used to thinking of energy in terms of watt-hours rather than volts. In a chemical reaction the total number of electrons (quantity of current) is known, so that the net electrical work (or energy) is:

$$nFE$$

where  $n$  is the number of electrons per molecule,  $F$  is the Faraday, which is 96,500 coulombs per equivalent, and  $E$  is the voltage. The oxygen over-voltage on copper at a current density of 0.001 amp/cm<sup>2</sup> has been reported to be 0.42 volts. Since 4 electrons are involved in the reduction of oxygen, the activation energy is  $4 \times 96500 \times 0.42$  or 162120 calories per mole.

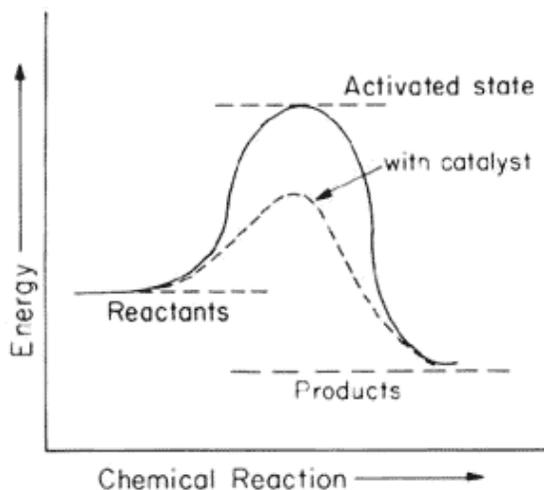


FIGURE 2. Energy of Activation

The significance of the activation energy is illustrated in Figure 2. The required activation energy acts as a barrier that must be overcome. The higher this barrier, the fewer molecules will have energies that equal or exceed this value and the slower the reaction will proceed. It should be noted, however, that even if the metal were a perfect catalyst (i.e. activation energy is zero), oxygen molecules in the vicinity of the cathode would become depleted and the rate of the corrosion reaction would still be limited by the relatively slow rate at which the oxygen molecules diffuse to the

surface of the metal.

It is instructive to make some changes in the galvanic cell and observe the results. A decrease in temperature causes current output to decrease 1 to 2% per degree F. Since the viscosity of water increases with a drop in temperature, the diffusion and migration of ions and molecules is retarded. When the electrolyte freezes, there is a dramatic decrease in current.

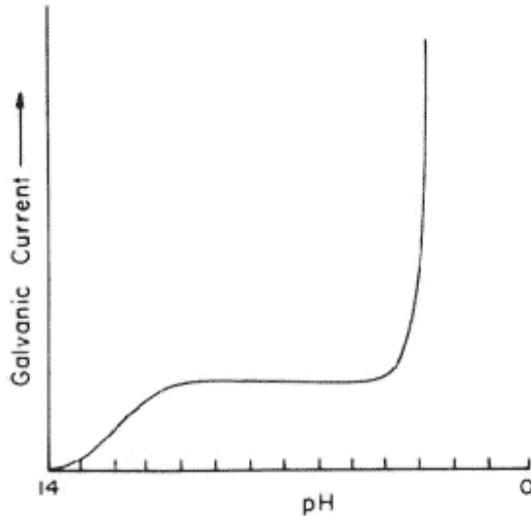
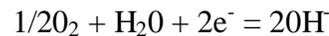


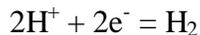
FIGURE 3. Effect of pH on the corrosion rate of iron.

Current increases as dissolved oxygen concentration is increased. This effect is very nearly proportional except in weak electrolytes. Current increases proportionately with salt concentration depending somewhat on the specific ions that are created when the salt dissolves. For example, sodium chloride will increase the current more than the same weight of sodium sulfate.

Except as it may affect the Langelier Index, pH has little effect over the ranges normally found in well waters (Figure 3). If the pH is above 10, the hydroxyl ion concentration is so high that it tends to reverse the cathode reaction:



At pH values below 4, hydrogen ion replaces oxygen as the oxidizing agent and the cathode reaction becomes:



From the fact that nearly all of the voltage drop in the galvanic cell occurs at the water cathode interface, the effects of changing the geometry of the cell may be predicted. If the anode and cathode are moved closer to each other, there is little increase in current. As the cathode is withdrawn from the solution, the current is found to be proportional to the cathode area that remains submerged. If the anode area is reduced, there is only a small decrease in current.

The practical consequences of these area effects are important. In nearly all commercial gate valves there are brass rings in the cast iron body, but because the brass cathode area is very small compared to the iron anode, galvanic corrosion is negligible. Note that a protective coating placed on the anode must be perfect, or very severe pitting will occur at any pinholes. On the other hand, if the cathode is coated with an insulating film, galvanic corrosion can be greatly reduced even with a relatively poor coating.

Figure 4 illustrates that, in a highly conductive electrolyte, corrosion will be greater and will extend for a considerable distance from the cathode, while in a poorly conducting electrolyte, corrosion will be localized near the cathode. Thus it is possible for perforation to occur more rapidly in the less-conductive solution although the total amount of corrosion is much less in the weak electrolyte.

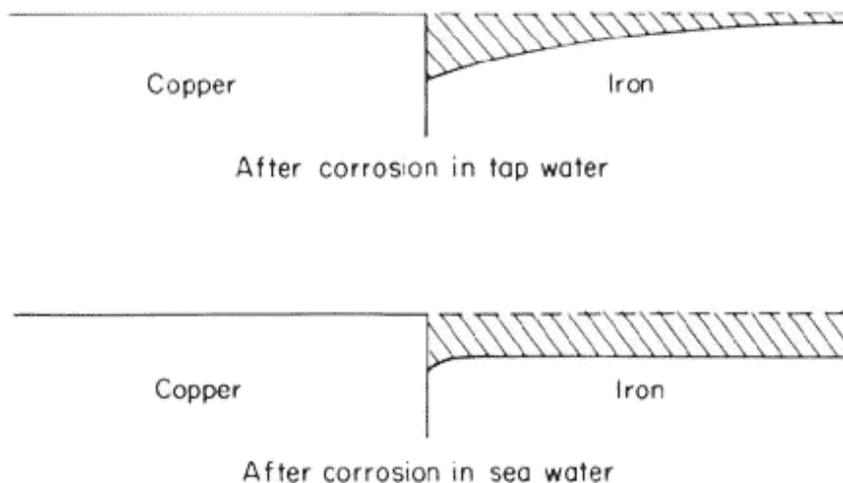
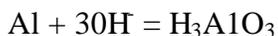


FIGURE 4. Relative distribution of corrosion in a weak electrolyte (tap water) and a strong electrolyte (sea water).

When the metals comprising the cathode are changed, the principal effect is to change polarization. If the copper cathode is replaced with stainless steel, for example, the initial current is about the same, but after a few hours the galvanic current from the stainless is only a small fraction of that from copper. Thus a stainless steel screen connected to a mild steel casing would cause far less corrosion on the mild steel than would a bronze or Monel screen.

Table I shows the galvanic series. This is similar to the electrochemical series shown in Table II, except that the latter is based on thermodynamically reversible reactions, which are not practically attainable. The galvanic series is supposed to represent what happens in the real world. As in the real world, however, there are some surprises. For example, although zinc is higher than iron in the table, at 140o F the potentials are reversed. This was first recognized in the early 1950's. Prior to that time it was standard practice to galvanize the interior of water heaters, supposedly protecting the steel, but actually causing more rapid failure. Although magnesium is above aluminum in both tables, it was found that severe attack of aluminum in the vicinity of magnesium rivets occurred in the hulls of flying boats made during World War II. Investigation revealed that the hydroxyl ions resulting from the reduction of oxygen attacked the aluminum:



You will note that aluminum is fairly high in the table and it may surprise you that Alcoa claims it "will not rust or rot". Aluminum holds up well when exposed to air, thanks to a continuous and highly adherent oxide layer, but is generally unsatisfactory in fresh water environments.

I have discussed the galvanic cell in considerable detail because it is well suited to explain the electrochemical nature of corrosion. However, the galvanic cell is responsible for only a small fraction of corrosion that occurs in potable waters.

TABLE I  
Galvanic Series

|                       |
|-----------------------|
| Magnesium             |
| Zinc                  |
| Aluminum (2S)         |
| Cadmium               |
| Aluminum (175T)       |
| Steel or Iron         |
| Cast Iron             |
| Lead-Tin Solder       |
| Lead                  |
| Nickel                |
| Brasses               |
| Copper                |
| Bronzes               |
| Stainless Steel (304) |
| Monel                 |
| Stainless Steel (316) |
| Silver                |
| Graphite              |
| Gold                  |

TABLE II  
Electrochemical Series

|           |
|-----------|
| Magnesium |
| Aluminum  |
| Zinc      |
| Chromium  |
| Iron      |
| Cadmium   |
| Nickel    |
| Tin       |
| Lead      |
| Copper    |
| Silver    |
| Gold      |
| Platinum  |

The principal cause of corrosion in water is the oxygen concentration cell. This very important mechanism has not been given the attention it deserves in most publications on corrosion, perhaps because it introduces an apparent anomaly: Oxidation of metal occurs at a site where there is no oxygen.

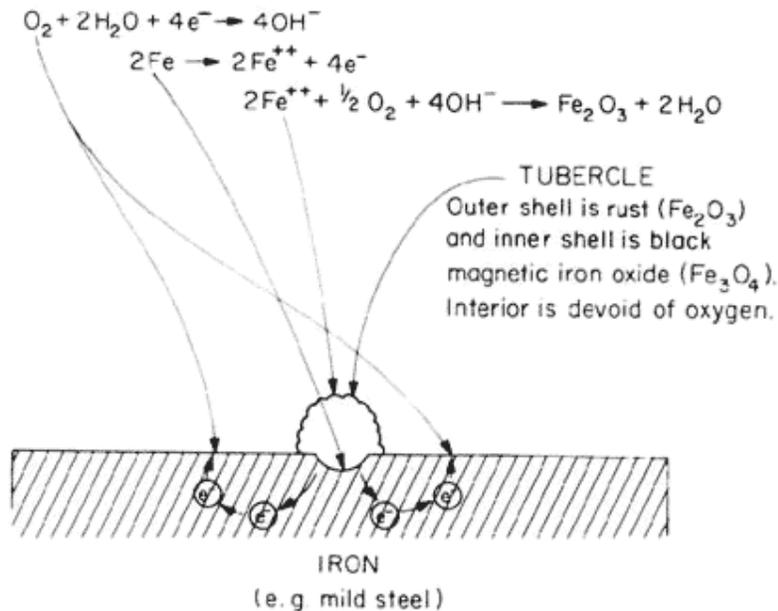


FIGURE 5. Oxygen Concentration Cell

Figure 5 depicts an oxygen concentration cell. Note that the chemical reactions involved are precisely the same as those that occur in a galvanic cell, and since voltage produced by the cell is determined by the chemical reactions, the potential of any oxygen concentration cell will be exactly the same as in a galvanic cell where the corroding metal is the anode. Polarization characteristics will depend on how this metal behaves as a cathode.

The oxygen concentration cell may be initiated by anything that

will shield a small area from the dissolved oxygen in the water, such as a grain of sand or a microbial colony. Once started, the cell becomes self-perpetuating. A pit forms that is covered with a crust of metal oxide, assuring there will be no oxygen under the tubercle that is formed.

When the corroding metal is iron or steel, an additional reaction occurs. The ferrous ions produced are oxidized to ferric hydroxide:



The interior of a tubercle contains a solution of ferrous chloride and sulfate ions in concentrations greater than those in the water. Hydrogen sulfide is occasionally present. The solution is slightly acid and may have a pH of approximately 6. This liquid is covered by a black inner crust consisting of hydrous  $\text{Fe}_3\text{O}_4$ , which, being magnetic, is attracted to the iron to form porous columnar fibers. The outer crust consists of reddish brown ferric hydroxide or hydrated ferric oxide. The flow of current protects the metal in the immediate vicinity of the pit. In ferrous metals, pits generally become inactive after a period of time. When this occurs, they no longer protect the metal in their vicinity, and new pits develop. Apparently the tubercles become so impermeable that ions cannot diffuse through, and since the solution inside must maintain electrical neutrality, no additional iron ions are formed.

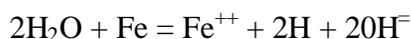
Pits in copper are nearly always well isolated, suggesting that, unlike tubercles formed in iron, the tubercle in copper, once formed, continues to be active.

When the pH of water is below 7, the rate of formation of  $\text{Fe}^{+++}$  from  $\text{Fe}^{++}$  and  $\text{O}_2$  is very much slower than at higher pH values. Hence tubercles are less likely to form, so that oxygen concentration cells are less likely to be self-perpetrating, and corrosion is more apt to be uniform.

Values of pH less than 7 are usually encountered in waters of low alkalinity and low dissolved solids. Under these conditions, uniform corrosion results. Corrosion may be severe in terms of total loss of metal, but in the absence of pitting, perforation will not be rapid and facilities often have reasonably long life. Nevertheless, these low-pH, low-alkalinity waters may be highly undesirable for drinking water supplies. Lead pipe and fittings are rapidly attacked and solder from copper pipe joints enters the water. Lead presents a health hazard in concentrations of only a small fraction of a part per million.

In wells, the portions of the casing and column above the water level are usually covered with condensate saturated with air. Since air contains carbon dioxide, the water has a pH of less than 7 and alkalinity and dissolved solids are for practical purposes equal to zero. Well casing subject to this uniform corrosion becomes so thin that failure occurs after periods up to a century.

Under these conditions, the classical corrosion reactions adequately explain the results. The lower pH values favor the reaction:



The atomic hydrogen then reacts with oxygen:



with HO-OH (hydrogen peroxide) as a likely intermediate. Note that these reactions are equivalent to those that have been described for the galvanic cells and the oxygen concentration cell. In all cases iron is oxidized to ferrous ions and electrons. The electrons react with oxygen and water to form hydroxyl ions. The principal difference is that, in uniform corrosion, the cathode and anode are separated by microscopic distances, while in galvanic and oxygen concentration cells, the anode and cathode may be separated by several millimeters.

Dezincification, although it occurs infrequently, is an interesting subject. Yellow brass alloy is replaced by porous copper. It was at first assumed that the zinc was selectively dissolved from the alloy, but it is now generally agreed that the entire alloy dissolves. Copper ions in solution find themselves more noble than the alloy, so they plate the surface, leaving a porous structure having very little mechanical strength. Dezincification occurs only in high zinc alloys, principally yellow brass (67% Zn - 33% Cu), and corrosion is usually caused by oxygen concentration cells or galvanic action. However, zinc is amphoteric and is attacked by hydroxyl ions:



In one large water system where pH was raised to a value greater than 9 by lime softening, operators encountered numerous failures of brass valve stems. Dezincification of these stems was attributed to the above reaction.

During an investigation of the occurrence of heavy metals from corrosion of household plumbing, it was found that generally the concentration of metals decreases as the plumbing ages. The one exception was cadmium from galvanized plumbing, which was not detected in relatively new homes, but was found in significant concentrations from galvanized plumbing over 50 years old. It was demonstrated that the zinc used to galvanize the pipe contained approximately a half of a percent of cadmium. When the Cd - Zn alloy dissolved, the dissolved

cadmium ions plated on the remaining alloy, thus gradually increasing the concentration of this toxic metal.

By now, if you have followed this discussion, you may be under the impression that all natural waters containing dissolved oxygen are severely corrosive. That this is not the case is due largely to the fact that many naturally occurring waters are capable of coating the cathode area of the metal with a thin layer of calcium carbonate. In order for this to occur, three conditions must be met: (1) the water must have a Langelier Index close to zero, (2) it must contain a significant bicarbonate ion concentration, and (3) it must be flowing over the metal surface.

Water has a Langelier Index of zero when it is in equilibrium with calcium carbonate [2]. When water is passed through a column of crushed limestone (a crystalline form of calcium carbonate), it has a negative index if some of the limestone is dissolved, a positive index if some calcium carbonate is precipitated, and a zero index if there is no change.

In chemical terms (See Appendix A) it can be shown that:

$$pH_s = \log K_2/K_s - \log (Ca) - \log (HCO_3)$$

where  $pH_s$  is the pH at which the water is just saturated with  $CaCO_3$ ,  $(Ca)$  and  $(HCO_3)$  are the concentrations of calcium and bicarbonate respectively,  $K_2$  is the second ionization constant of carbonic acid, and  $K_s$  is the solubility product of calcium carbonate. The values of the constants depend upon the temperature and the degree of mineralization (ionic strength) of the water.

At room temperature (25°C) and moderate mineralization (400+mg/l total dissolved solids) the above equation becomes:

$$pH_s = 11.85 - \log (Ca) - \log (HCO_3)$$

where both the calcium and bicarbonate are expressed as calcium carbonate.

To illustrate the use of the above equation, consider a typical ground water in the Santa Clara Valley. Calcium hardness is 100 mg/l and alkalinity is 200 mg/l. Both hardness and alkalinity are usually expressed as  $CaCO_3$ . Hence the saturation pH is:

$$11.85 - \log (100) - \log (200) = 11.85 - 2 - 2.3 = 7.55$$

This is close to the pH value actually found in the water. Since the coastal mountains surrounding the valley contain dolomite (a calcium magnesium carbonate), one would expect the ground water to be saturated with calcium carbonate.

At pH values below 8, essentially all the alkalinity is in the form of bicarbonate. If the pH is significantly above 9, most of the alkalinity is in the form of carbonate and hydroxyl.

The Langelier Index is defined as  $pH - pH_s$ . Thus, if the pH of water having a zero index is increased, it will have a tendency to precipitate calcium carbonate.

As previously noted, hydroxyl ion is produced by the cathode reaction in the electrochemical cell. Furthermore, electrons are involved in this reaction. Electrons flow through the metal and will not flow through water. Thus the reaction must occur at the water-metal interface.

Next consider the flow of water through a pipe. It can be shown that if the flow in gallons per minute exceeds the radius of the pipe in inches, the Reynolds number (at room temperature) will exceed 1,700 and flow will be turbulent. Thus, in practice, laminar flow is very uncommon in metallic pipes unless the diameters are very small.

When flow is turbulent there is always a layer of laminar flow adjacent to the pipe wall (Figure

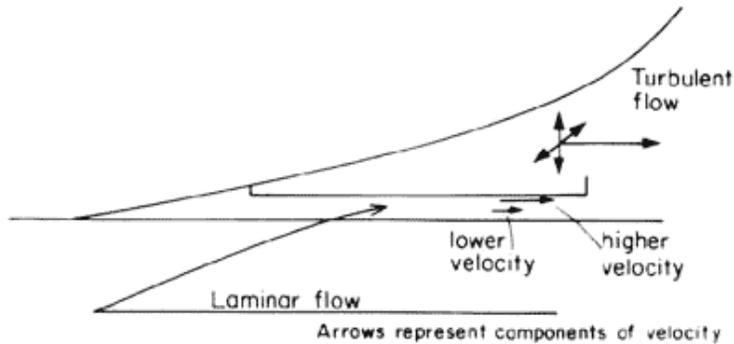


FIGURE 6. Velocity profile of flowing water next to a wall with turbulent flow.

6). The only way hydroxyl ions from the cathode reaction can escape from the pipe wall is by diffusion through this layer. Under typical conditions of flow, the laminar layer is very thin. For example, in a steel pipe, 8" dia., carrying 400 gpm of water at room temperature, this layer is less than 0.01" thick. The hydroxide ions, trapped in this relatively small volume of water, react with the calcium and bicarbonate in the water:



to form a coating of calcium carbonate. The turbulence in the main body of flow rapidly replenishes the calcium and bicarbonate ions to the laminar layer, but to reach the metal surface they must diffuse through the laminar layer.

Table III shows that the bicarbonate ion has the lowest diffusion coefficient of any of the chemical species involved in the formation of calcium carbonate. In order for the calcium carbonate film to form on the cathode, it is necessary that the water in the laminar layer be supersaturated with calcium and carbonate ions. Since the carbonate ion has a higher rate of diffusion than the bicarbonate ion, supersaturation can be maintained in the laminar layer only if the water in the turbulent stream is nearly saturated, so that nearly as many carbonate ions diffuse into the laminar layer as diffuse out of it. The calcium carbonate film on the cathode surface almost stops the corrosion reaction because the diffusion of oxygen to the metal-electrolyte interface is greatly retarded.

| Chemical Species   | $\text{Cm}^2/\text{sec} \times 10^5$ |
|--------------------|--------------------------------------|
| $\text{OH}^-$      | 5.28                                 |
| $\text{O}_2^-$     | 2.6                                  |
| $\text{CO}_3^{--}$ | 2.29                                 |
| $\text{Ca}^{++}$   | 1.59                                 |
| $\text{HCO}_3^-$   | 1.46                                 |

Diffusion coefficient at infinite dilution at 25°C

Thus calcium carbonate film formation is a dynamic process - chemically because the hydroxyl ion is produced by the corrosion reaction itself, and physically because it forms only where there is turbulent flow. Many authorities treat the protective calcium carbonate film as if it were a coat of paint rather than the result of the corrosion reaction itself. In 1956, Werner Stumm [3] suggested that the calcium carbonate film was brought about by the cathode reaction, and he presented experimental evidence that showed significant corrosion mitigation by these films even when the Langelier Index is zero or only slightly positive. This important paper has not received the attention it deserves.

When Professor Langelier introduced the concept, it was widely accepted that corrosion would be inhibited in water having a positive index. Shortly thereafter, several water systems reported having corrosion problems even with Langelier indices as high as + 1.0, and the value of the index as an indicator of corrosion was seriously questioned. Gradually it was recognized that the

failures occurred in those systems where the water had excessively high pH values. A purely empirical index called the Ryznar Index was proposed [4]. When used in conjunction with the Langelier Index, its effect is to severely limit the pH of the saturated water. T. E. Larson expressed the opinion, based on experience, that water should have a slightly positive Langelier Index, and that ideally the pH should not exceed 8.6 [5]. These limits on pH have the effect of assuring that nearly all the alkalinity is in the form of bicarbonate.

Currently it is fashionable to use the "Calcium carbonate precipitation potential" which is the amount of supersaturation in mg/l [6]. This may be calculated graphically from the Caldwell-Lawrence diagram [7], or, more easily, by using the computer program given in Appendix B. The mathematical basis for the program is given in Appendix A. The program is also useful for water softening calculations.

If the calcium carbonate precipitation potential is too high, pipelines and perforations will be plugged with calcium carbonate. Precipitation occurs where velocity is highest, because that is where turbulence supplies ions at the greatest rate. This brings to mind another common misconception:

*"Calcium carbonate can be carried in solution in ground waters in proportion to the amount of dissolved carbon dioxide in the water. The capacity of water to hold carbon dioxide in solution varies with the pressure - the higher the pressure, the more carbon dioxide will be held. When water is pumped from a well, the water table is drawn down to produce the necessary gradient or pressure differential in the water-bearing formation to cause water to flow into the well. The hydrostatic pressure in the deeper portions of the water-bearing formation is thus decreased, the greatest change being at the well. Because of the reduction in pressure, more or less carbon dioxide is released from the water. When this occurs, the water is often unable to carry in solution its full load of calcium carbonate and part of this slimy material is then precipitated in the sand adjacent to the well screen. " [8]*

It is true that the solubility of a gas increases with pressure, but if the water is originally saturated at a given pressure, no gas will be released until the pressure drops below that value. It is extremely unusual to find a water that is supersaturated with carbon dioxide at atmospheric pressure. Such a water will fizz like a seltzer water when exposed to the air. Let us assume a well water is saturated with carbon dioxide at atmospheric pressure, the screen slots form perfect venturi throats, and are 100 feet below the pumping level.

The lowest absolute pressure in the screen slots would be, in feet of water:

$$H = 34 + 100 - V^2/64.4$$

In order to release carbon dioxide, the absolute pressure would have to become less than 34 ft. and the velocity would have to be greater than 80 ft./sec.

Another cause of incrustation that occurs in the absence of corrosion is deposition of iron oxide or manganese dioxide resulting from the growth of iron bacteria. As with calcium carbonate deposits, growths are most prolific at points of high velocity. I vividly remember the first time I examined shaft and column from a water-lubricated pump that had been removed from a well infested with a growth of iron bacteria. The shaft, rotating at nearly 1800 rpm, was coated with a

growth at least 3/4" thick, while the growth on the column was less than 1/4" thick. It was surprising that the centrifugal force had not thrown the growth off the shaft.

It may be helpful to consider the corrosive effect of specific chemical species that are reported in mineral analyses of water. Sometimes theory conflicts with conventional wisdom which, hopefully, has been acquired through experience. Part of the problem results from woefully incomplete data. Water analyses seldom report dissolved oxygen concentration, which is certainly the most important constituent in considering corrosivity.

Since corrosion is an electrochemical reaction, one would expect highly conductive waters to be more corrosive than those of lower conductivities. Often this is true. Sea water is generally much more corrosive than fresh water. On the other hand, very pure waters such as distilled waters and steam condensate are generally considered to be highly corrosive.

Water containing large concentrations of carbon dioxide is considered to be highly corrosive, even to copper. Carbon dioxide is not an oxidizing agent. It reacts with water to form carbonic acid:



However, carbonic acid is a very weak acid that does not attack copper, although there is some attack of iron, particularly in hot water. Water that contains large amounts of carbon dioxide is usually highly conductive, with a negative Langelier Index, so that if it contains any dissolved oxygen, it is very corrosive. Thus, waters with concentrations of carbon dioxide of over approximately 40 mg/l are usually corrosive.

Hydrogen sulfide is an acid, but it is even weaker than carbonic acid. Furthermore, it will react with dissolved oxygen, so if it is present in an aquifer, it signals the complete absence of oxygen. Waters containing hydrogen sulfide are therefore singularly free from corrosion. If such a water is aerated to remove the objectionable odor of hydrogen sulfide, it may become highly corrosive.

Sulfate ion is a very strong oxidizing agent, whose rate of reaction is fortunately so slow that its oxidation potential has no practical significance in corrosion. Its reactions may be catalyzed by *Sporovibrio Desulfuricans*, a sulfate-reducing bacteria which has been responsible for severe external corrosion of pipe passing through peat bogs. If severe corrosion has been noted in wells where water contains hydrogen sulfide, the possibility of sulfate-reducing bacteria should not be overlooked. As with high concentrations of carbon dioxide, a strong odor of hydrogen sulfide may be an indicator of corrosive water.

It is generally accepted that bicarbonate retards corrosion, sulfate and nitrate are neutral, and chloride accelerates corrosion. The beneficial effect of bicarbonate is probably largely a result of the role played by this ion in forming calcium carbonate films over the cathodes. The conductivity contributed by these ions in dilute solution is:

|                  |   |       |
|------------------|---|-------|
| Cl               | = | 2.14  |
| SO <sub>4</sub>  | = | 1.54  |
| NO <sub>3</sub>  | = | 1.15  |
| HCO <sub>3</sub> | = | 0.715 |

microhms/cm per mg/l. At higher concentrations normally found in ground water, all of these values are decreased, but sulfate decreases more rapidly than the others because of the divalent charge. There is much evidence to suggest that in addition to its effect on conductivity, chloride ions specifically accelerate pitting in ferrous metals, particularly the stainless steels.

One is tempted to speculate that one reason for the corrosive effect of excessive chloride concentrations may be that the reaction



is reversible. The equilibrium constant is such that it goes almost to completion as written. However, when the chloride concentration is excessive, some chlorine may be present, and since the overvoltage of chlorine (and other halogens) is negligible, oxidation of iron occurs.

Normal velocities (1 to 5 ft./sec.) are generally beneficial. Higher velocities often cause a combination of corrosion and erosion that may be very severe. Copper tubing appears to be particularly susceptible to erosion-corrosion which results in elongated undercut pits that are easily recognized at velocities of 5 to 10 ft./sec., depending on the quality of the water. Ferrous metals require even higher velocities. If the velocities are great enough to cause the absolute pressure to drop below the vapor pressure of water, cavitation will result. Such velocities are attained only by pump impellers, ship propellers, and similar equipment.

The term "electrolysis" should be used to describe corrosion caused by the flow of stray electric current where the source of the current is external to the structure. Severe damage has resulted from improper grounding of electric railways and electric welding systems and other facilities using direct current. Improper grounding of alternating current systems may cause corrosion but it is generally accepted that the corrosion resulting from the flow of AC is only about 1% of that caused by the same flow of DC.

Although the internal corrosion of water pipes is often attributed to improper grounding of an electrical system, it is doubtful if that is ever an important cause of corrosion. For example, the superintendent of a New Jersey water utility recently reported an instance of blue water caused by the corrosion of copper pipe, which he blamed on improper grounding. He demonstrated that there was an AC flow of 7 amps through the copper water line in a home where there was enough copper in the water to impart a blue tinge. A 7-amp flow is evidence of grossly improper grounding, so he could hardly be blamed for assuming that the corrosion was caused by electrolysis.

However, calculation based on the known electrical resistivities of copper, and water in this system, showed that the flow of current through the water could be no greater than .29 micro amps. The amount of corrosion caused by this small flow of AC could not account for the observed corrosion.

Serious electrolysis has probably occurred on the outside of the buried portions of the copper tube. Significant internal corrosion could occur only in the immediate vicinity of high-resistance joints where a significant flow of current could be carried by the water. A properly soldered copper joint has an even lower resistance than an equivalent length of copper pipe.

Unfortunately, the dissolved oxygen and other chemical characteristics of the water were not reported, so the actual cause of the corrosion could not be determined.

One of the most common general ways to mitigate corrosion is by means of cathodic protection. Cathodic protection may use either impressed currents or galvanic currents. The direct current for an impressed current system is usually obtained from the transformer-rectifier combination that is designed to provide the necessary current at the proper voltage. These systems have been used to prevent external corrosion of well casing and pipelines, but are not practical to prevent internal corrosion of these structures because the protective currents will travel only a very few pipe diameters from the anode. Impressed current cathodic protection is frequently used to prevent corrosion of steel water tanks. Sacrificial anodes of duriron (a high silicon alloy of iron) are highly satisfactory. The cathode reaction produces hydroxyl ion, so that if the water contains calcium and bicarbonate ions in moderate concentrations, a film of calcium carbonate is formed that keeps the current required for protection to quite low values.

Cathodic protection may also be provided by galvanic currents. The structure to be protected is electrically connected to a less noble metal. Zinc and magnesium anodes have been used to protect steel pipelines from external corrosion. Zinc in the form of a coating on steel (galvanizing) is used extensively to protect the steel from corrosion in fresh water. The zinc will protect the steel until it is nearly all gone. Galvanizing is very satisfactory under moderately corrosive conditions, but since the zinc corrodes readily, it does not last long in severely corrosive environments.

Protective coatings of paint, coal tar, or asphalt may be worse than no coating at all because pinholes in the coating permit pits to form that may result in perforation.

Coatings of Portland cement are highly satisfactory even though there may be hairline cracks in the coating. It appears that water entering hairline cracks acquires a very high pH from solution of the cement so that no corrosion occurs.

Bare steel is anodic to steel coated with cement. This caused severe damage to water and gas lines when subdivisions using concrete slab floors were first built shortly after World War II. Inadvertent metallic connections between the reinforcing mesh used in the homes and water or gas piping caused very severe corrosion currents to flow.

Water treatment is usually the most economical means to mitigate corrosion in municipal supplies, although it is not a practical means of protecting well screens or casing. The most common treatment is to adjust the pH to a slightly positive Langelier Index, by the addition of sodium hydroxide or preferably lime.

In industrial cooling towers, brine for refrigeration or cooling water for internal combustion engines requires rather high concentrations (up to 3,000 mg/l) of sodium chromate to prevent corrosion. Sodium chromate is poisonous and cannot be used in drinking water.

Municipal supplies are occasionally treated with zinc salts. Zinc carbonate is less soluble than calcium carbonate so that under the proper values for pH and alkalinity, zinc is capable of forming cathode films much as calcium does.

Sodium silicate in concentrations of 12 to 16 mg/l (as SiO<sub>2</sub>), has been used to prevent corrosion in hot water systems. Molecularly dehydrated phosphates such as metaphosphate and tetrphosphate have also been used to prevent corrosion in potable waters.

Under many conditions such as occur in well screens, the only practical means of mitigating corrosion is to use a corrosion-resistant material. Generally, the 18-8 stainless steel of the 300 series will withstand corrosive water unless the chloride concentration exceeds 500 mg/l.

A final means of nullifying the effects of corrosion may be to increase the thickness of the structure. It has been shown that pit depth P, in ferrous metals buried in soil, may be related to time of exposure t, by the following equation [9, 10]

$$P = K t^n$$

where the value of K depends upon the environment and n for soils takes on the value of 1/6, 1/3, 1/2 and 2/3. The same relationship may be expected to hold for water, but n should be 1/6 where the cathode reaction produces a protective film and 1/3 where it does not. Thus, if the thickness of the structure is doubled, the time required for a pit to penetrate will be 8 times as great or 32 times as great, depending upon whether or not a cathode film is formed.

In conclusion, it should be noted that there is not much that can be done about corrosion that is occurring in a well. While it is often practical to treat the water leaving the well to reduce corrosivity, it is obviously impractical to treat the water before it enters a well. However, if a well in a specific area has failed prematurely due to corrosion, the well driller can prevent the same thing from occurring in a replacement well either by selecting aquifers that produce less corrosive water or by using corrosion-resistant materials.

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# Appendix A

## Derivation

$(Ca^{++})_o$  = initial  $Ca^{++}$  Conc - moles/l

$(Mg^{++})_o$  = initial  $Mg^{++}$  Conc - moles/l

$A_o$  = initial Alkalinity - equiv/l

$(pH)_o$  = initial pH

Using the formula given by Lowenthal and Maria, the following equilibrium constants may be calculated for water at any temperature and ionic strength.

$K_1$  first ionization constant  $H_2CO_3$

$K_2$  second ionization constant  $H_2CO_3$

$K_w$  ionization constant  $H_2O$

$K_s$  solubility product  $CaCO_3$

$K_{mg}$  solubility product  $Mg(OH)_2$

$$(1) (H^+)_o = 10^{-(pH)_o}$$

$$(2) A_o = (HCO_3^-)_o + 2(CO_3^{--})_o + (OH^-)_o - (H^+)_o$$

$$(3) (CO_3^{--})_o = K_{2o}(HCO_3^-)_o / (H^+)_o$$

$$(4) (OH^-)_o = K_w / (H^+)_o$$

Substituting (3) and (4) in (2)

$$(5) (HCO_3^-)_o = \left( \frac{A_o - K_w}{(H^+)_o} + (H^+)_o \right) \left( \frac{(H^+)_o}{(H^+)_o + 2K_2} \right)$$

Total carbonic carbon  $C_o$  by definition:

$$(6) C_o = (CO_2)_o + (CO_3^{--})_o + (HCO_3^-)_o$$

$$(7) C_o = \frac{(HCO_3^-)_o(H^+)_o}{K_1} + \frac{K_2(HCO_3^-)_o}{(H^+)_o} + (HCO_3^-)_o$$

$$(8) C_o = (HCO_3^-)_o \left( \frac{(H^+)_o}{K_1} + \frac{K_2}{(H^+)_o} + 1 \right)$$

Substituting (5) in (8)

$$(9) C_o = \left( \frac{A_o - K_w}{(H^+)_o} + (H^+)_o \right) \left( \frac{(H^+)_o}{(H^+)_o + 2K_2} \right) \left( \frac{(H^+)_o}{K_1} + \frac{K_2}{(H^+)_o} + 1 \right)$$

Thus  $C_o$  can be calculated from the pH, alkalinity, and equilibrium constants.

Let X be the moles of  $CaCO_3$  precipitated from one liter of

a supersaturated water to reach equilibrium. ( $-X$  is moles that will dissolve in an undersaturated water). After equilibrium has been reached

$$(10) C_e = C_o - X$$

$$(11) (Ca^{++})_e = (Ca^{++})_o - X$$

$$(12) A_e = A_o - 2X$$

where subscript "e" denotes concentration after equilibrium has been established. Using the same logic used in deriving equation 9.

$$(13) C_o = \left( A_o - 2X - \frac{K_w}{(H^+)_e} + (H^+)_e \right) \left( \frac{(H^+)_e}{(H^+)_e + 2K_2} \frac{(H^+)_e + K_2}{K_1} + 1 \right) + X$$

which can be solved for X

$$(14) X = \frac{C_o - (A_o + Y_3) Y_1 Y_2}{1 - 2 Y_1 Y_2}$$

where  $Y_1 = (H^+)_e - K_w/(H^+)_e$

$$Y_2 = 1 + (H^+)_e/K_1 + K_2/(H^+)_e$$

$$Y_3 = \frac{(H^+)_e}{(H^+)_e + 2K_2}$$

also, at equilibrium

$$(15) (Ca^{++})_e (CO_3^{--})_e = K_s$$

$$(16) \frac{(H^+)_e (CO_3^{--})_e}{(HCO_3^-)_e} = K_2$$

Eliminating  $(CO_3^{--})_e$

$$(17) \frac{(Ca^{++})_e (HCO_3^-)_e}{(H^+)_e} = \frac{K_s}{K_2}$$

Solving for  $(H^+)_e$

$$(18) (H^+)_e = \frac{K_2 (Ca^{++})_e (HCO_3^-)_e}{K_s}$$

Substituting for  $(Ca^{++})_e$  and  $(HCO_3^-)_e$

$$(19) (H^+)_e = \frac{K_2}{K_s} \left( (Ca^{++})_o - X \right) \left( A_o - \frac{K_w}{(H^+)_e} + (H^+)_e \right) \left( 1 + \frac{(H^+)_e}{K_1} + \frac{K_2}{(H^+)_e} \right) \left( \frac{(H^+)_e}{(H^+)_e + 2K_2} \right)$$

Equations 14 and 19 establish the relationship between  $(H^+)_e$  and  $X$ .

Equations 14 and 19 each have two unknowns,  $(H^+)_e$  and X. They contain so many terms that direct simultaneous solution appears to be impractical.

Using a method of successive approximation, a value for  $(H^+)_e$  is assumed and the corresponding value for X is calculated from equation 14. Using the value of X, the value of  $(H^+)_e$  is calculated from equation 19. If this value is not sufficiently close to the initially assumed value, a new value for  $(H^+)_e$  is assumed and the process is repeated.

If the solubility product for  $Mg(OH)_2$  is exceeded during the course of the above calculations, corrections must be made in both the alkalinity and magnesium concentrations.

$$(20) \text{ If } (Mg^{++})_o > K_{mg}/(K_w/(H^+)_e)^2$$

then

$$(21) Z = (Mg^{++})_o - K_{mg} ((H^+)_e/K_w)^2$$

$$(22) (Mg^{++})_e = (Mg^{++})_o - Z$$

## Appendix C

### Water Samples

If possible, obtain sample bottles and directions for taking samples from the laboratory. Make arrangements to coordinate the collection, transportation, and testing of the samples so as to minimize delay in testing for pH, bacteria, and other constituents where time of standing may affect results.

When taking bacteriological samples, the bottle must be sterile and care must be exercised not to contaminate either the bottle or sample. Allow the sample tap to flow smoothly for at least one (1) minute before collecting sample. Do not flush at high rate first since this will disturb sediment in the sample pipe. Avoid touching the inside of the bottle cap or the lip of the bottle.

Samples for mineral analysis must be taken in clean bottles with plastic (non-metallic) caps. Allow only enough air space for thermal expansion so as to minimize gain or loss of carbon dioxide. Avoid splashing or entraining air bubbles during collection.

When collecting samples from wells, temperature should always be taken, because this may provide a clue as to the average depth of the producing aquifers. The thermometer should have the scale engraved on the glass and the graduations should be such that you can estimate the reading to the nearest degree F. Allow the water to overflow a small plastic container (a polystyrene coffee cup is ideal). Immerse the thermometer in the cup and read the temperature after the reading has been constant for a minute or more.

Samples for dissolved oxygen are not difficult to take, but you must have the following equipment and reagents:

1. A 1/4" O. D. polyethene tube that can be connected to the sample tap.
2. A special sample bottle with a tapered ground-glass, stopper. It should have a capacity of approximately IV 250 ml.
3. Three small (35 to 100 ml) bottles equipped with screw-on rubber bulb dispensing pipettes . The pipettes should discharge approximately 0.5 ml when the bulb is squeezed (an ordinary eye dropper is satisfactory).
  - a. The first bottle contains a 40% solution of manganous sulfate  $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$ .
  - b. The second bottle contains alkaline iodide reagent consisting of 70 gm of KOH and 150 gm KI diluted to 100 ml.
  - c. The third bottle contains concentrated sulfuric acid. This is one of the most dangerous chemicals in common use and must be handled with great care.

Fill the sample bottle with water, using the plastic tube immersed almost to the bottom of the special bottle. Allow it to overflow so that 4 to 10 volumes have been displaced. Turn off the sample tap and withdraw the plastic tube, being careful to avoid introducing any air in the sample. Immerse the eyedropper containing the manganous sulfate under the surface of the water and add 1 ml (2 squirts) of manganese sulfate reagent. Next add 1 ml of alkaline iodide reagent, taking pains to assure that no air bubbles are introduced when the reagent is added. Insert the stopper without trapping any air bubbles and mix the solution by rapidly inverting the bottle. A heavy floc of manganese hydroxide will form at this point. Allow this floc to settle for three (3) or four (4) minutes, remove the stopper carefully, add 1 ml of concentrated sulfuric acid, again insert the stopper and mix by inverting the bottle.

The sample now contains a solution of iodine that is chemically equivalent to the initial dissolved oxygen. The solution is stable and can be transported to the laboratory for exact determination.