

CORROSION FUNDAMENTALS

Presented at the

Cathodic Protection Design Seminar

Sponsored by the

**Technical University of Nova Scotia
Toronto, Ontario**

February 1990

by

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TECHNICAL PAPER #11124



**CORROSION
SERVICE**

CORROSION FUNDAMENTALS

Elements known to the ancients were given Latin names which were abbreviated. Iron was called Ferrum in Latin which was abbreviated to Fe. Copper was called Cuprum shortened to Cu, etc. More recently discovered elements are usually abbreviated by using the first two letters in the name, for instance Aluminum (Al), Argon (Ar). In some cases, the first and some subsequent letter is used to avoid confusion with another element eg. Arsenic (As). In general, these symbols must be committed to memory.

A REVIEW OF ATOMIC STRUCTURE, VALENCY AND FORMATION OF IONS

Atoms were originally thought to be the smallest particle into which an element could be subdivided that would still retain the physical and chemical characteristics of the element itself. Modern atomic theory suggests a much more complicated entity which, of necessity, will be simplified in what follows.

Each atom has a positively charged nucleus around which electrons orbit. The positive charges on the nucleus are exactly balanced by a number of electrons which orbit around the nucleus. An atom has no net electrical charge and is therefore electrically neutral. If an electron can, somehow, be added to or taken away from a neutral atom, the atom exhibits an electrical charge, negative if an electron has been added and positive if an electron were taken away. An atom thus electrified is called an ion and the process is called ionization.

Atomic nuclei are complex in themselves but for our purposes we consider them to contain protons which are positively charged particles and neutrons which are without charge but have

the same weight as a proton. The simplest of all atoms is the hydrogen atom which consists of a single proton neutralized by a single electron orbiting around the nucleus, Hydrogen is the lightest element. Heavier elements have larger nuclei and correspondingly greater numbers of protons and neutrons. For every positively charged proton on the nucleus a corresponding electron will orbit about this nucleus. The electrons orbit at different distances from the nucleus and occupy a series of shells which are given letters by chemists for identification purposes. The innermost shell is K the next shell is L, etc. Heavier elements have up to seven shells of orbiting electrons. Elements can be arranged on a table called the Periodic Table. Here each element has a number called its "atomic number" which corresponds to the number of electrons in orbit (or conversely the number of protons in the nucleus). For example, Hydrogen has an Atomic Number of 1 and Uranium an Atomic Number of 92. The elements are listed in order of their Atomic Numbers and also in "Periods" in which all elements have the same number of electron shells. The Periods are numbered from 1 to 7. A periodic table is shown in Figure 1 below.

Period	1A	2A	3B	4B	5B	6B	7B	← 8B →	1B	2B	3A	4A	5A	6A	7A	ZERO		
1	1 H 1.008															2 He 4.003		
2	3 Li 6.939	4 Be 9.012									9 B 10.81	10 C 12.011	11 N 14.007	12 O 15.999	13 F 18.998	14 Ne 20.18		
3	11 Na 22.99	12 Mg 24.31	TRANSITION ELEMENTS								15 Al 26.98	16 Si 28.09	17 P 30.97	18 S 32.06	19 Cl 35.45	20 Ar 39.96		
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.1	45 Rh 101.1	46 Pd 106.4	47 Ag 107.87	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.7	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.0	84 Po (210)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226.1	89 Ac (227)															
LANTHANIDES				58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0	
ACTINIDES				90 Th 232.0	91 Pa (231)	92 U 238.0	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)	

FIGURE 1

PERIODIC TABLE OF ELEMENTS

When atoms react with one another, it is logical to assume the first contact is made between outer shells. It is also logical to suspect that physical and chemical properties of elements are related to electrons in the outermost shells of elements. Examination of the Periodic Table shows a group of elements on the right hand side of the table which are called the inert gases. The more common of these, Helium, Neon and Argon are well known from their commercial uses. Helium has two electrons in its "K" shell which "completes" the shell. The other elements in this group have eight electrons in the outermost shell which again is considered complete. From experience, it has been found that elements whose outer shell electrons when shared add up to eight have a strong affinity for one another and form stable compounds made up of at least 2 atoms. For example, Iron, Atomic No. 26 (Period 4) has two electrons in its outer orbit. Oxygen, Atomic No. 8 (Period 2) has six electrons in its outer orbit. Bring them in contact with one another, they share their outer orbital electron to achieve the stable value of 8 and form iron oxide. Sodium, Atomic No. 11 (Period 3) has one electron in its outer orbit. Chlorine, Atomic No. 17 (Period 3) has 7 electrons in its outer orbit. Bring these elements into contact and again they share their outer orbital electrons to achieve the stable value of 8 to form Sodium Chloride. Sometimes elements combine to form compounds that involve more than two atoms. For example, Magnesium, Atomic No. 12 (Period 3) has two electrons in its outer orbit whereas Chlorine as indicated above has seven outer orbital electrons. Here a magnesium atom combines with two chlorine atoms to form a molecule of magnesium chloride. The shared electrons considered to be in the outer orbital again have a value of 8.

In general, metals corrode by giving up electrons in their outermost orbits to non-metallic corrodents that use these electrons to complete their outer shells that are deficient of few electrons only. The electrons in the outer orbits are called valence electrons. The word valence is used in the sense of "combining ability". Most people recognize the formula for common table salt NaCl. In the example given above, it is observed that Chlorine is deficient an electron to

“complete” its outer electron shell and that Sodium had a single electron in its outer shell which it could share with the Chlorine. If both Chlorine and Sodium have a valence of 1, this knowledge can be used to deduce the valence of other elements if the proportions in which they combine are known. Magnesium chloride is denoted by the formula MgCl_2 where two Chlorine atoms combine with one Magnesium atom. It can be inferred from knowledge of the valence of Chlorine that Magnesium has a valence of two. Although an indication of valencies can be taken from information on a Periodic Table, some elements have several valencies and in addition there are groups of atoms called radicals which exhibit valencies which do not appear on the Periodic Table. In general valencies should be memorized. The theory underlying the combining of atoms to form molecules is much more complicated than indicated in this brief review. A modern approach is covered by Cartwell and Fowler ⁽¹⁾.

PROPERTIES OF IONS

Properties of atoms depend on their electronic structures. If electrons are added to or taken away from an atom, the atom exhibits an electrical charge corresponding to the relative imbalance that exists between the positive charge on the nuclei and the total charge represented by associated electrons. This process is called ionization. As would be expected, an ion differs markedly from the atom from which it was obtained. Ions are formed readily in aqueous solutions when compounds such as salts are dissolved or when metals are corroded. When NaCl is dissolved in water its ions Na^+ and Cl^- are completely dissociated from one another. In fact a crystal of common salt is made up of an orderly array of ions arranged such that no net electrical charge is discernible. Dissolving or solvating these ions permit them to move about freely. Since ions carry electrical charges they will migrate in an electrical field and are responsible for the transfer of electrical charges in aqueous solution. Very pure water is a poor electrical conductor (good

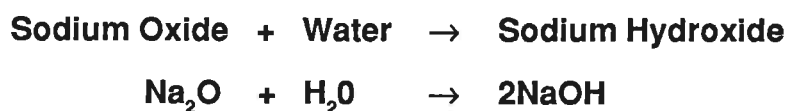
insulator?) and it is the presence of ionized substances in solution that enhances its ability to conduct electricity. Since pure water and water containing dissolved NaCl look the same, we can assume the Na^+ ion and the Cl^- ion are colourless. If copper chloride (CuCl_2) is dissolved in water, the salt dissociates into Cu^{++} and 2Cl^- ions and a pronounced blue colour is noticed. Since we have already determined that Cl^- ion is colourless then the Cu^{++} ion is responsible for the blue colour. Chemical properties also change when ions are produced. Chlorine is a yellow acrid poisonous gas in its elemental form whereas the chloride ion Cl^- has none of these properties.

ACIDS AND BASES

If a gas hydrogen chloride is dissolved in water, a very strong acid is produced. HCl (hydrochloric acid) ionizes into H^+ and Cl^- ions. Since Cl^- ions also exist in solutions of table salt and seem innocuous then the acidic properties must be due to the H^+ ion. Similarly when sulphur trioxide is dissolved in water, sulphuric acid is produced. H_2SO_4 ionizes into 2H^+ and SO_4^{--} . Again it can be demonstrated that the acidic properties are due to the H^+ ion and not the SO_4^{--} ion. The H^+ ion in water is always associated with a water molecule and is more correctly thought of as a hydronium ion H_3O^+ . The concentration of hydronium ion in solution can be determined using a special glass electrode that is sensitive to hydronium ion concentration and determining its potential versus a standard reference electrode. A relationship exists between the potential read by a voltmeter between these two electrodes and the logarithm of the hydrogen ion concentration. The strength of an acid solution is expressed in pH units which represent the negative index of the hydrogen ion concentration. For example at pH 0, the concentration of hydrogen ion is 1 gram-mol per litre. At pH 7 (neutral) the concentration is 10^{-7} gram moles of H^+ per litre. Low pH numbers indicate acid solutions. High pH numbers indicate a very small concentration of H^+ ions, hence no acidity. In summary, an acid is any substance that will yield hydronium ion in an

aqueous solution. These substances are nearly always oxides of non-metals.

When concentrations of hydronium ion are less than 10^{-7} gram ions per litre (pH7), the solution is said to be basic. Strong bases can have pH's of 14 or more. Oxides of the light metals form strong bases when dissolved in water:



Sodium Hydroxide dissociates into Na^+ and OH^- ions. Experience with the Na^+ ion in common salt solutions does not indicate any properties of a base therefore we can conclude that basic properties are due to the OH^- or hydroxyl ion. Metals can be defined as those elements whose oxide when dissolved in water will produce a base.

Hydronium ion has a sharp sour taste (vinegar, lemon juice) whereas hydroxyl ion has a flat soapy taste (milk of magnesia).

METALLIC CORROSION

Most metals, with the exception of a few noble metals known to the ancients, do not exist in nature in their metallic form but rather as compounds or ores from which they must be extracted by the addition of considerable amounts of energy. Gold, silver and copper were used by the ancient people since they could be found in their native state. The smelting of those metals most easily reduced from their ores was discovered perhaps 5,000 years ago. Modern steels were not produced until the development of the blast furnace and Bessemer converter in the mid-to-late

nineteenth century. Twentieth century metals such as aluminum, magnesium, tantalum and zirconium require electrical energy in their extraction. Since corrosion can be thought of as the reverse of the smelting or electro-winning process, one would expect that corrosion would spontaneously destroy metals at a rate proportional to the difficulty of wresting them from their ores. Since corrodents attack the surfaces of metals by well known rules of chemistry, it is often true that the nature of the corrosion product can slow down the corrosion rate. It has been said that no metal could exist exposed to the atmosphere were it not for a tightly adherent layer of corrosion product on its surface.

Corrosion can be defined as the interaction of a metal (or other substance) with some element in its environment to produce a corrosion product that lacks the desirable properties of the original material. Although corrosion can take place at higher temperatures in the absence of liquid water, and since this dissertation is leading into a discussion on cathodic protection, it will be restricted to aqueous corrosion involving metals only. Corrosion manifests itself as general wastage, pitting attack leading to perforation of pipes, tankage and ships, weld attack, intergranular attack, stress corrosion cracking, discolouration and loss of aesthetics, production of toxic or unwanted corrosion products, pyrophoric destruction, etc. The corrosion processes that will be discussed herein are spontaneous that is the conversion of a metal to corrosion product will result in the release of energy.

Michael Faraday studied the amount of electric current necessary to convert a metal into its ions (corrosion product). He found that if the amount of metal converted was equal to the atomic weight of the metal in grams divided by the valence of the metal that the amount of charge transferred was 96500 coulombs. This value was called Faraday's Equivalent.

If a metal is converted to corrosion product, energy is released which relates to the weight of metal converted. The released energy is denoted by ΔG and is called Gibb's Free Energy. Gibb's Free Energy is related to electric cell potential E and the amount of reacted material n with F (Faraday's Equivalent) the proportionality constant:

$$\Delta G = -nEF$$

As discussed above, n is equal to the number of gram atomic weights of metal corroded divided by the change of valence of the metal for that reaction (two valencies are possible for some metals). If E is in volts and F is in coulombs per equivalent, the ΔG is expressed in joules. E is the potential measured across the external terminals of a corrosion cell. In non-aqueous corrosion ΔG can be determined by calorimetry. The cell potential becomes zero when the metal is totally converted to corrosion product.

A corrosion cell consists of two electrodes immersed in an aqueous solution connected externally by a conducting path. The solution must be able to conduct electricity for example if very high purity water were used, it is unlikely that corrosion would be initiated. The simplest cell to describe is one in which the electrodes are made of two different metals one with a good corrosion resistance (such as copper) and one with a known tendency to corrode such as iron. The surface of the aqueous solution is in contact with the atmosphere and hence will contain some dissolved oxygen. In such a cell the iron will corrode and is called the anode, the copper will not corrode and is called the cathode. The intervening conducting aqueous solution is called the electrolyte. Anodic (corrosion) reactions involve the dissolution of iron as an iron ion. This ion is usually the divalent ferrous ion denoted Fe^{++} . The electrons that were associated with this ion remain in the parent metal. Very few of these ions can enter the solution without a corresponding reaction taking place at the copper electrode in which electrons transferred from the anode

via the external conducting path are consumed in a cathodic reaction in this case (neutral solution) involving oxygen. This reaction is expressed in chemical shorthand shows the consumption of electrons to produce hydroxyl ions in solution.



The electrical potential measured across the cell terminals when the external circuit is interrupted corresponds to the E in the Gibb's Energy formula. The rate of reaction at the anode exactly corresponds to the rate of reaction at the cathode. The anode reaction is referred to as an oxidation reaction and is characterized by a change in valence of the metal in the anode from Fe^0 to Fe^{++} . In general oxidation is said to take place where the valence of an atom or ion becomes more positive. The cathode reaction is referred to as a reduction reaction and is characterized by a change in valence of a reacting species in the negative direction for example in the plating of copper Cu^+ becomes Cu^0 . Oxidation occurs when a metal atom gives up one or more valence electrons to the anode and becomes a positively charged ion. Reduction occurs when a positively charged ion accepts electrons from the cathode or when a neutral atom accepts electrons from the cathode to become a negative ion. The cell reactions described thus far occur in what are called primary cells since they react spontaneously and create electrical energy according to Gibb's equation. Note that the energy is produced by the dissolution of the anode which is a corrosion process and that the cathode does nothing more than provide an electrode surface at which electrons can be picked up to achieve the reduction of ions in solution. There is a class of cells called electrolysis cells in which electrodes are chosen which are either inert or of the same metal. When a cell with inert electrodes is powered by an external voltage source, oxidation reactions take place at the electrode where positive charges enter the solution as in the primary cell but the oxidized species are in the electrolyte itself. Typical of such a cell would be one set up in secondary school chemistry classes in which platinum electrodes are used together with a

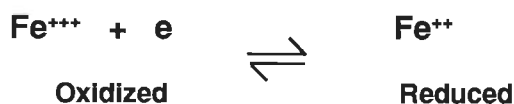
battery to electrolyse water into its components hydrogen and oxygen. Electrolysis cells are used in many other ways to produce special compounds, to produce metals from molten salts, to refine metal and to achieve corrosion protection by means of anodic and cathodic protection.

Although a metal may act as a cathode when combined with another metal in a particular cell, it will perform as an anode when combined with a metal less reactive than itself. It is possible to produce cells of different metal combinations and measure the cell potential E referred in the Gibb's equation taking note of the polarities of the electrode. Such an experiment will permit the arrangement of common metals and alloys in a common electrolyte (say seawater) in an order in which the most electronegative metals are at the top of the list and the most electropositive (least electronegative) are at the bottom of the list. Such lists are called "galvanic series" and can be found in chemistry texts. A shortened version is shown below Table 1.

NEGATIVE ACTIVE OR ANODIC	MAGNESIUM AND MAGNESIUM ALLOY
	ZINC
	CHROMIUM
	COMMERCIAL PURE ALUMINUM
	CADMIUM
	[STEEL OR IRON CAST IRON
	LEAD
	TIN
	[BRASSES COPPER BRONZES
	STAINLESS STEEL
POSITIVE NOBLE OR CATHODIC	SILVER

TABLE No.1 - GALVANIC SERIES OF SOME COMMERCIAL METALS AND ALLOYS IN SEAWATER

Any metal in this series when coupled to a metal below it in the series will be the anode of a primary cell. In general the greater the separation of metals on this list, the greater the expected value of cell potential E . In a properly constructed cell the greater the value of E , the greater the corrosion rate at the anode. The potential across the terminals of a primary cell depends upon many variables in addition to the materials of the electrodes, for this reason, potentials seldom appear on galvanic series in publications. A more scientific arrangement of metallic elements called the Electrochemical Series is available in texts. In this series, cell potentials are measured between pure metals and a platinum electrode over which hydrogen is being bubbled. The electrolyte has a standard composition involving ions of the metal being measured against the hydrogen electrode and the temperature of the cell is held constant at 25° C. The potential of these special cells is called the standard potential and it is denoted as E_o . The electrochemical series report the electrode potentials with respect to the hydrogen electrode to at least three significant figures. It is also possible by using inert electrodes to determine the electrode potential at which certain oxidation and reduction reactions take place in the electrolyte. These potentials called “redox” potentials are usually measured versus the hydrogen electrode and represent the potential adopted by an inert electrode in contact with both oxidized and reduced forms of a system in equilibrium. For example, consider the equilibrium between ferrous and ferric ions in solutions:



Depending on the direction of this reaction electrons are either taken from the inert electrode or deposited upon it. The redox potential is that adopted by the inert electrode when the reaction is in equilibrium. If the electrode potential is made more negative than this equilibrium value (ie. more electrons are available) then the above equation produces more reduced species and conversely.

It is possible to measure cell potentials by inserting a reference electrode into the cell and measuring the anode to reference potential and the cathode to reference potential separately and summing them algebraically to arrive at the cell potential. The preferred scientific reference is the hydrogen electrode and it is considered as the datum point (or zero) for measurement of the potentials of metals in the Electrochemical Series. Other references of a more practical construction are in common use such as the “saturated calomel electrode” the “silver-silver chloride electrode” and the “copper-copper sulphate electrode”. Heights of buildings, mountains and aeroplanes are referenced to datum points, it is clear that the datum point must be referenced to make the numerical values understandable. The height of a building is usually referenced to the street level. The height of mountains and aeroplanes is understood to be referenced to “mean sea level”. If the corrosion potential of a metal is reported, then it becomes absolutely necessary to mention the reference to which it is being measured. Reference electrodes or “half” cells usually consist of a pure metal in a controlled environment adjacent to the metal itself. Contact with the electrolyte of the cell into which the reference is inserted is usually accomplished using a conductive “bridging” solution. The bridging solution is kept pure by interposing a porous membrane or plug between the bridging solution and the electrolyte of the system being measured. In many cases, a hydrostatic head is maintained in the reference cell such that a small flow of the bridging electrolyte enters the cell electrolyte as a further safeguard against reference cell contamination. The bridging electrolyte is usually chosen to reduce or eliminate liquid-to-liquid junction potentials caused by unequal mobilities of ions in the respective solutions that may lead to charge separation at the semi permeable membrane interface. Reference electrodes that have saturated electrolytes are easier to maintain than those that have some specified dilution. The saturated calomel reference electrode consists of a pool of mercury which is contacted by a platinum wire. The mercury pool is in intimate contact with a paste of mercurous chloride and mercury. This paste is in contact with a saturated solution of potassium chloride. This reference has a potential more positive than the hydrogen reference by 0.242 volts at 25° C. Calomel

references are also made with 0.1 normal and 1.0 normal potassium chloride solutions which have smaller temperature coefficients than the saturated reference. The saturated copper-copper sulphate reference consists of a pure copper rod in a saturated solution of copper sulphate. This reference is easily maintained and made of inexpensive materials, its potential is more positive than the hydrogen electrode by 0.316 volts and has a temperature coefficient similar to saturated calomel. The silver-silver chloride reference electrode can be used in seawater without any bridging electrolyte. The reference electrode consists of a silver rod attached to a silver gauze impregnated with silver chloride. This electrode stabilizes quickly in seawater to a potential of 0.25 volts more positive than the hydrogen reference. When taking measurements of electrode potentials with any of the above mentioned references the value measured is really a cell potential of a cell made up of the reference half cell and the electrode and its environmental electrolyte half-cell. For this reason reference electrodes are often referred to as half-cells. Since it is usual to perform potential measurements with very high resistance voltmeters, cell potentials are usually free of voltage drops associated with current flow in the metering circuit. Some common reference electrodes and their potentials with respect to the hydrogen electrode are shown in Table 2 below.

Electrode	Cell	Potential to SHE In Volts at 25°C	dE/dT In V/°C
0.15 Calomel	Hg/Hg ₂ Cl ₂ /KCl (0.1N)	0.334	-0.7 x 10 ⁻⁴
Saturated Calomel	Hg/Hg ₂ Cl ₂ /KCl (Sat))	0.242	-7.6 x 10 ⁻⁴
Silver-Silver Chloride	Ag/AgCl/KCl (0.1N)	0.288	-6.5 x 10 ⁻⁴
Silver-Silver Chloride	Ag/AgCl/Seawater	0.25	--
Copper Copper Sulphate	Cu/CuSO ₄ /CuSO ₄ (Sat)	0.316	-9.0 x 10 ⁻⁴

TABLE No.2

When a specific reference electrode is used, it is usual to report the measured voltage with respect to that electrode, that is the reference electrode is considered to be zero or datum point for that series of measurements.

If two metals are selected that are some distance apart on the galvanic series, say iron and copper and immersed in a beaker of tap water to which a little common salt has been added to improve its conductivity, this cell will have an open circuit potential of about half a volt. If a variable resistor is placed between these electrodes in the external circuit and a milliammeter is placed in series with this resistor then a variable corrosion current can be allowed to flow depending on the value of the resistance placed in the circuit. This experimental cell can be further embellished with two reference electrodes one placed adjacent to the iron anode and one placed adjacent to the copper cathode with suitable high resistance voltmeters connected between each electrode and its adjacent reference electrode. This arrangement is shown in Figure 2 below.

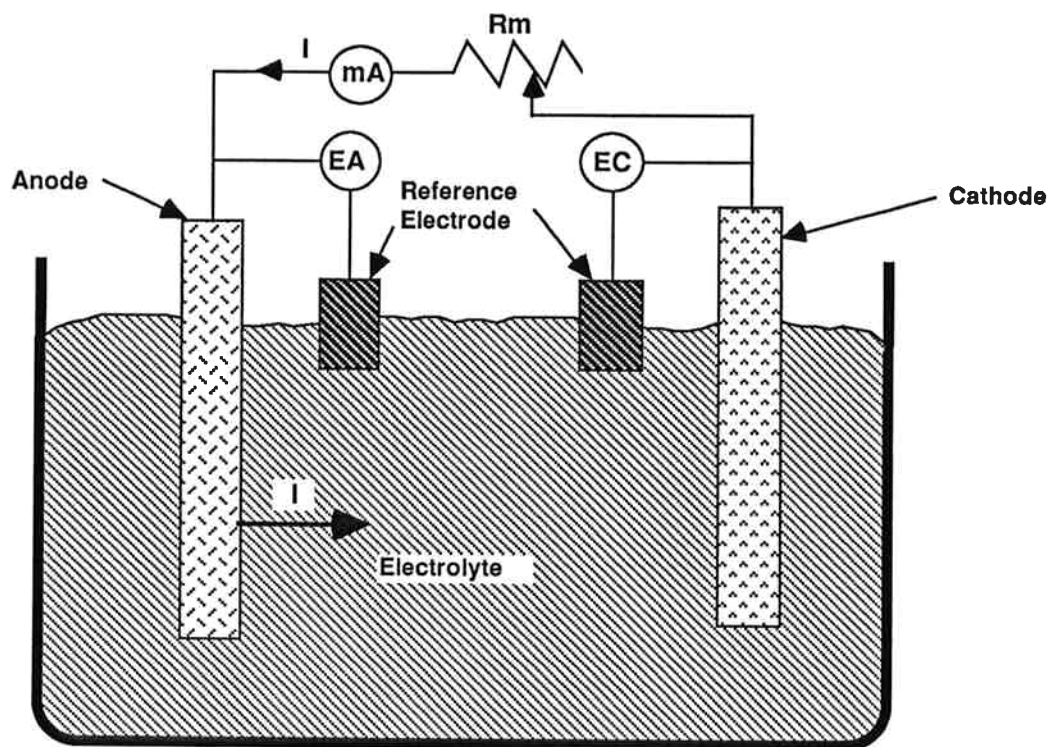


FIGURE 2

If the reference electrode chosen were calomel (saturated) and the switch in the external circuit were opened, the iron anode would be negative about 0.4 volts to the reference and the copper cathode would be positive about 0.1 volts to its reference indicating that the open circuit potential of this cell would be 0.5 volts as postulated with 0.4 volts contributed by the iron anode and 0.1 volts by the copper cathode. If a hydrogen reference electrode had been chosen 0.242 volts would have been subtracted from the potential contribution of the iron which would now appear to contribute 0.158 volts and the same 0.242 volts would have to be added to previous value of the potential contribution of the copper cathode which now becomes 0.342 volts. These two half-cell potentials still add up to 0.5 volts. This can be confirmed by placing a high resistance voltmeter across the terminals of the cell. The cell potential is independent of the references used in its measurement. Individual readings between reference electrodes and immersed metals are useful to compare changing conditions at the metal surface and are not useful in an absolute sense.

When the switch is closed and the resistance in the external circuit is reduced, a current flows in the external circuit that will be indicated on the milliammeter. The size of this current depends on a number of factors, the most obvious being the size of the resistance in the external circuit which in this example can be varied by the experimenter.

If this were the only factor affecting the flow of current in this cell as the resistance approached zero the current would become very large as indicated by Ohm's Law. Since only modest currents flow even under short circuited conditions, there must be other factors limiting this current value. These factors, of which there are several, are lumped into a term called polarization. This term can be broken down into three types of polarization.

1. Resistance polarization

2. Concentration polarization
3. Activation polarization

Resistance polarization is caused by the flow of current through the resistance of the electrolyte within the cell and disappears immediately when the cell is opened in the external circuit.

Concentration polarization is due to changes in concentration of reactants or products in the electrolyte adjacent to the anode and cathode and manifests itself as an opposing voltage within the cell that persists after the cell current ceases. Activation polarization also appears as a voltage opposing the cell potential and is due to the difficulty of electron transfer at the electrode-electrolyte interface. Like the voltage drop through a resistor, it does not persist after the cessation of cell current.

The net effect of these three factors is the decrease of potential across the terminals of a cell when increasing currents flow through it. This is shown in Figure 3 below:

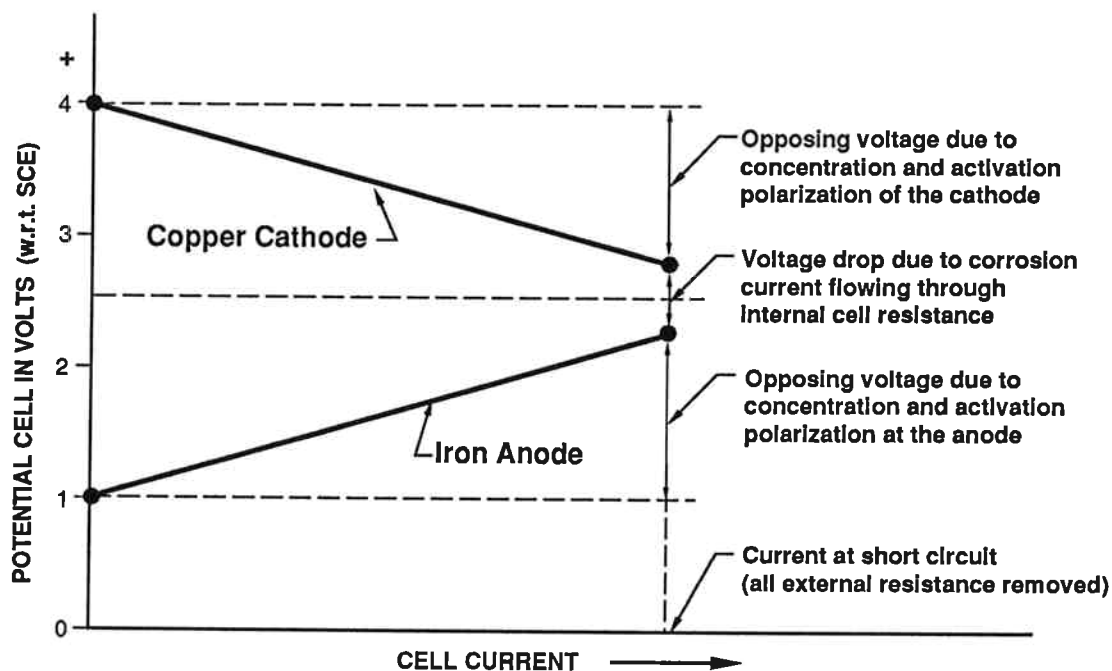


FIGURE 3

Curves plotting electrode potential against corrosion current are called polarization curves. In the above example, the internal cell resistance component is small (due to the addition of salt). If this internal resistance component were large as would be the case in fresh potable water, the corrosion current would be reduced as would be the size of the opposing voltage due to concentration and activation effects.

THE ELECTROCHEMISTRY OF CORROSION

If a simple galvanic cell as shown in Figure 2 is connected to a load, the electrode attached to the negative terminal of the cell corrodes. This electrode is identified as the anode of the cell. The reactions at the anode surface (corrosion) involve the ionization of the metal atoms:



Here a metal atom at zero valence gives up two electrons to become an ion exhibiting two positive charges. Any reaction in which the valence moves in the positive direction is described as an oxidizing reaction. The current flowing in the external circuit between the cell terminals determines the rate of dissolution of the anode. As previously mentioned Faraday determined that a charge transfer of 96500 coulombs would result in the dissolution of one atomic mass of electrode material divided by the change of valence for the electrode process. An ampere is the transfer of one coulomb per second hence coulombs transferred are determined by the product of amperes and time in seconds in which current flowed.

In summary the corrosion process involves an oxidation process in which a metal atom becomes an ion:



This is a corrosion process and occurs at the anode of the cell.

For an oxidizing reaction to occur a corresponding reduction reaction must take place. In a galvanic cell this reaction occurs at the cathode which is attached to the positive terminal of the cell. The electrons transferred in the external circuit are available at the surface of the cathode to react with oxidized species in solution. These species are ions with positive charges which plate onto the cathode surface and accept sufficient electrons from the cathode to neutralize their positive charges. In galvanic cells the cathodic reaction is generally limited to the reduction of H^+ ions in acid solutions and the reduction of oxygen in oxygenated acid solutions and the reduction of oxygen in neutral or basic solutions. These reactions are as shown below:

- (1) $2H^+ + 2e \rightarrow H_2\uparrow$ in acid solutions (\uparrow denotes gas evolution)
- (2) $4H^+ + O_2 + 4e \rightarrow 2H_2O$ in oxygenated acid solutions
- (3) $2H_2O + O_2 + 4e \rightarrow 4OH^-$ in neutral solutions

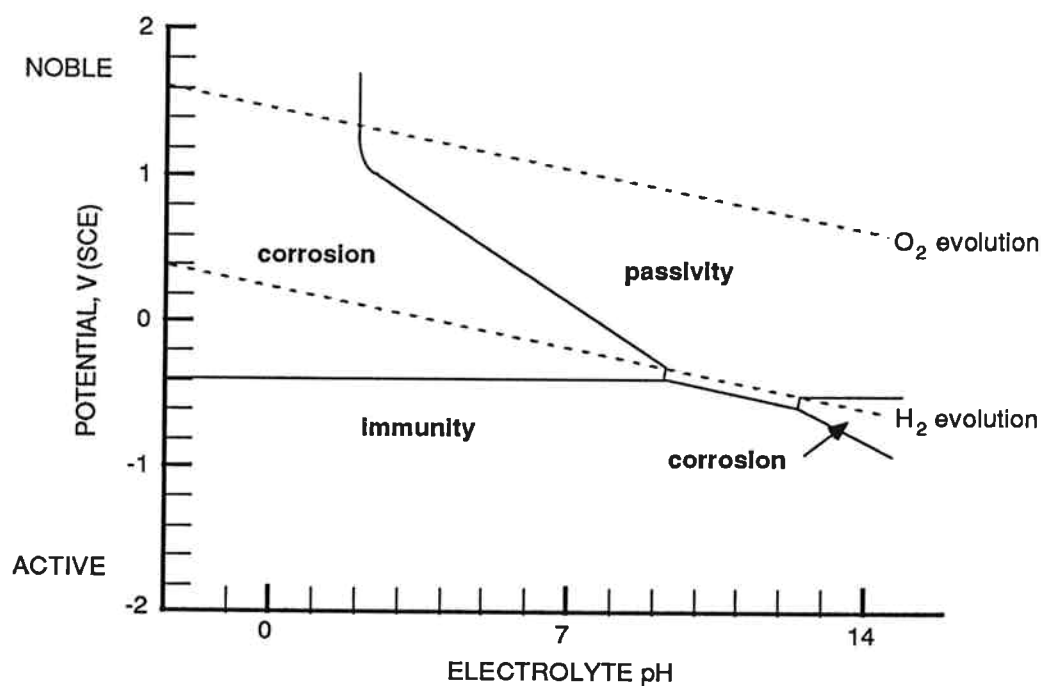
There two other reduction reactions that can take place at a cathode:

- (4) $Fe^{+++} + e \rightarrow Fe^{++}$ metal ion reduction
- (5) $Cu^{++} + 2e \rightarrow Cu$ the plating out of a metal

Since the corrosion process also involves a corresponding reduction process which in turn depends upon the pH of the electrolyte and oxygen availability and to a lesser extent on the presence of reduceable ions in solution. If any of these available cathodic processes can be eliminated or slowed down, there will be a reduction of corrosion rate at the anode. For instance, the neutralization of an acid condition will eliminate reaction (1). Note that reaction (2) accepts twice as many electrons as reaction (1) hence the removal of oxygen from an acid will lessen its

corrosivity. Reaction No. (3) can be eliminated if oxygen is not available. This is done in boiler water where the pH is adjusted to virtually eliminate the H^+ ion and the oxygen is then removed by scavengers.

Pourbaix created a diagram with electrode potentials on the ordinate and pH on the abscissa. By postulating small concentrations of corrosion product, he was able to calculate boundaries between domains of corrosion and immunity for different metals. He published an Atlas ⁽²⁾ of these diagrams. A simplified diagram for iron is shown in Figure 4 below.



Simplified Pourbaix Diagram for Steel

FIGURE 4

Since the boundaries shown on this diagram are derived from thermodynamic considerations alone, they indicate authoritatively when corrosion will not take place but give no indication of corrosion rates where corrosion is thermodynamically possible. In the domain identified as

passivity it is possible, under ideal circumstances, to find mild steel coated by a protective film of corrosion product that essentially prevents the corrosion of iron. A metal in such an environment has a polarization curve that shows a characteristic active-passive transition. In the normal way an anodic polarization curve would appear as shown in Figure 5.

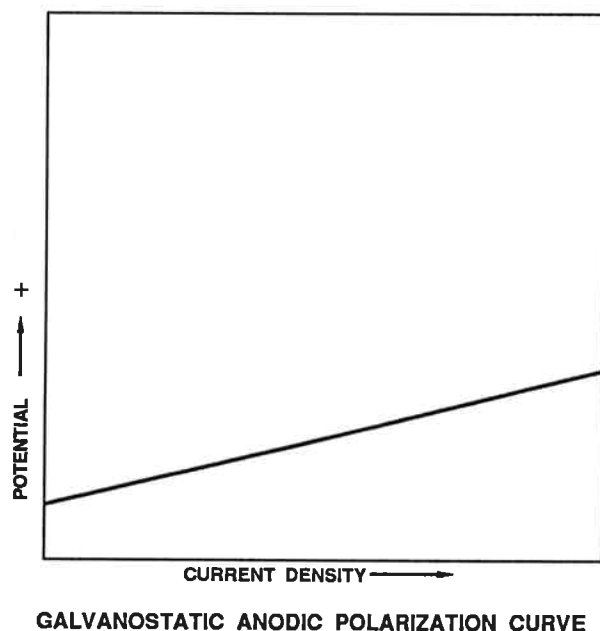


FIGURE 5

CMS-1006

This curve is produced by immersing the electrode under examination in a suitable electrolyte and with the use of a counter electrode in the same electrolyte, a DC power source connected between the electrodes and a means of controlling the current in increments, points along the curve can be determined. It is found that with some metals and electrolytes, an area of instability occurs where a very small increase of current causes a large instantaneous change of potential. This phenomenon is shown in Figure 6.

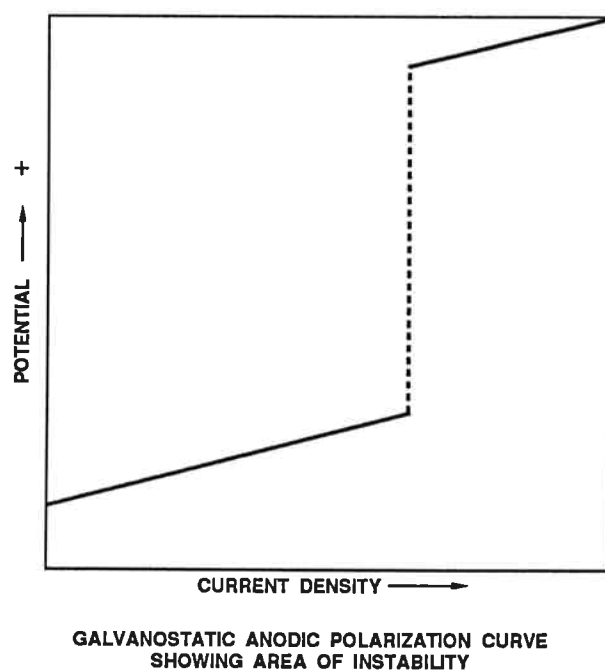


FIGURE 6

CMS-1007

This unstable electrode potential range can be studied by using a potentiostat. This instrument incorporates a DC power supply and a feedback control system that can hold an electrode at a preset potential by automatically adjusting the magnitude of the current being discharged or collected by the electrode under examination. Using this system of control the electrode potential becomes the independent variable and the current the dependent variable. Electronic plotters permit the recording of rapid current changes and curves such as those shown in Figure 7 are produced. It should be noted that the convention adopted in North America is contrary to mathematical convention that suggests the independent variable be plotted on the abscissa. The North American method of plotting makes it easier to overlay potentiostatic and galvanostatic plots or to compare them to potential-pH diagram where potentials are plotted on the ordinate.

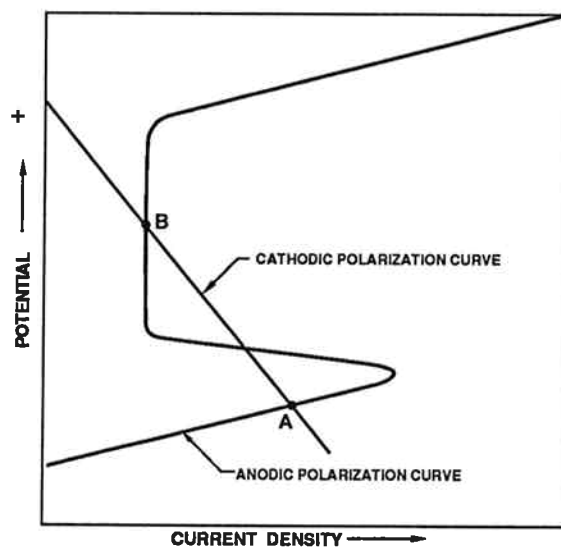


FIGURE 7

This particular curve is always obtained for a metal electrolyte system that shows instability under galvanostatic analysis. In Figure 8, this curve can be broken up into areas that are descriptive of the condition of the electrode metal when held in those potential regions and examined after a period of time.

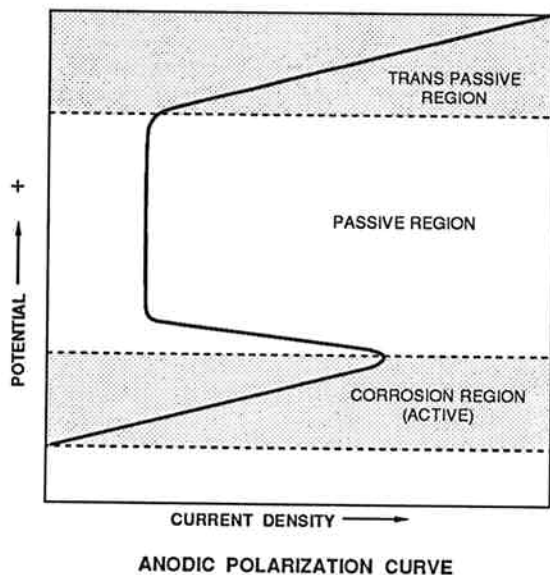


FIGURE 8

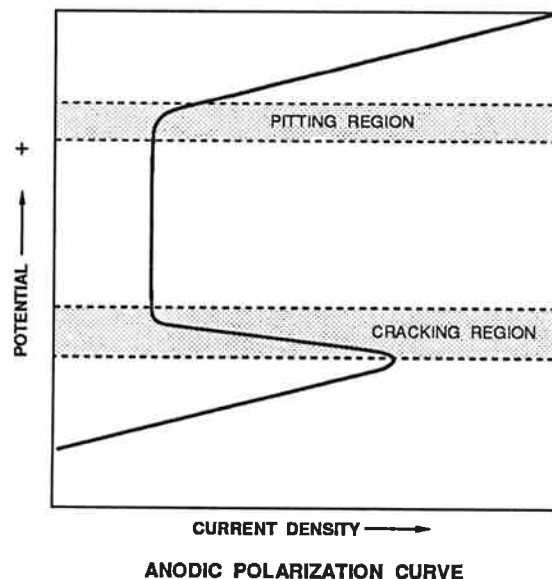
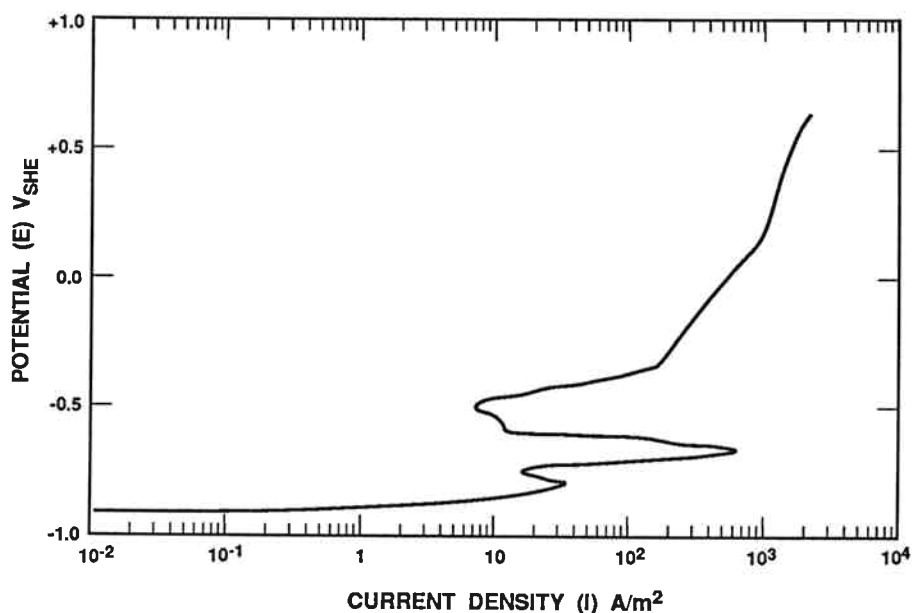


FIGURE 9

The main regions shown in Figure 8 can be further divided into sub-regions identified as pitting and cracking regions as shown in Figure 9. The cathodic region would be shown to the left of the ordinate on Figure 8 at potentials more electronegative than that shown at the intercept with the ordinate.

Metals that show anodic polarization behaviour as shown in Figures 8 and 9 are said to be capable of active-passive transition. Some metals show this behaviour only in specific electrolytes. In general metals that are normally passive such as stainless steels would have polarization curves of this general shape if activated or moved into trans-passive regions. Mild steel in high pH solution or in concentrated sulphuric acid will also show this behaviour.

Actual polarization curves are usually plotted with the current on a logarithmic scale expressed as current density. Figure 10 shows an actual polarization curve taken in a pulping liquor using a mild steel electrode.



ANODIC POLARIZATION BEHAVIOR OF
MILD STEEL IN $NaOH+Na_2S$ SOLUTION

FIGURE 10

Since corrosion rate is directly related by Faraday's equivalent to the current discharged from the electrode, examination of Figure 10 suggests that mild steel in the passive range would exhibit a corrosion rate of more than one order of magnitude less than that anticipated if potentials were in the corrosion or active region.

A Pourbaix Potential-pH diagram is produced in Figure 11 showing the relationship between this diagram and an anodic polarization curve showing an active-passive transition. Note that the region of immunity stretches across the bottom of the diagram and indicates the potential range in which an electrode will not corrode ie. it is thermodynamically stable.

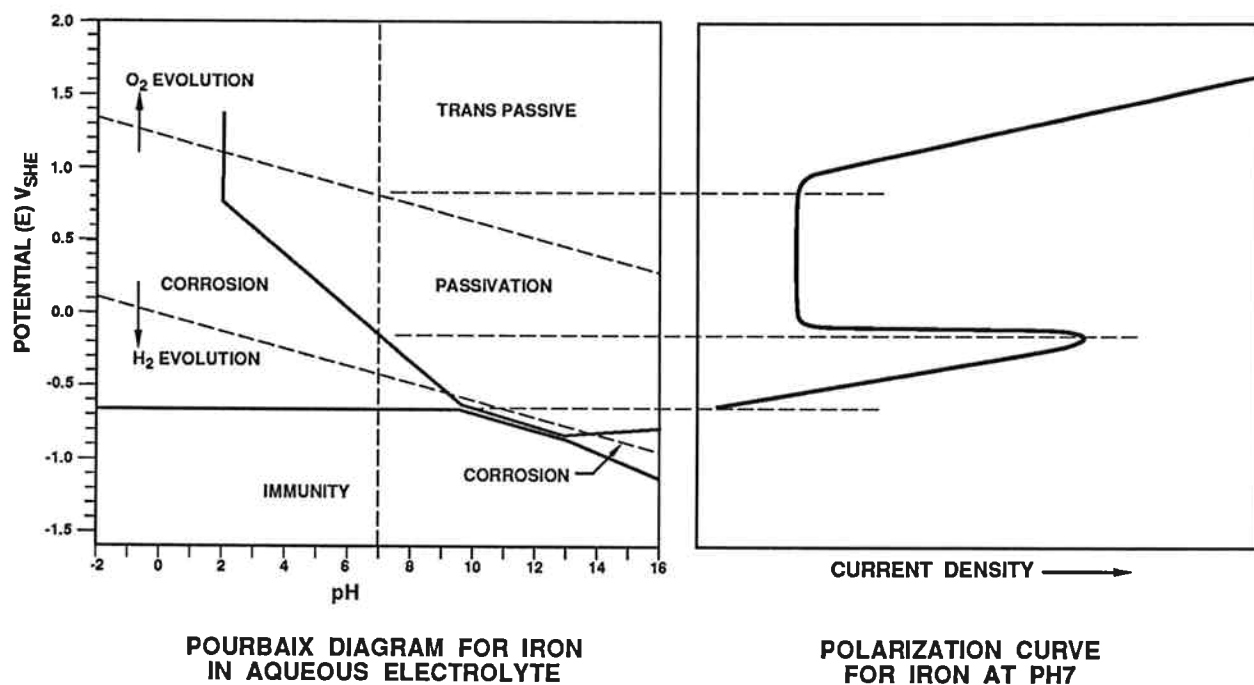


FIGURE 11

Thermodynamics treat only the possibilities of immunity or passivity. Although it is thermodynamically possible to render iron immune from corrosion at pH1, it is practically impossible. Enormous current densities are required to shift potentials in the negative direction since an

electrode reaction takes place before the immunity boundary is reached in which large volumes of hydrogen are released at the electrode surface.

CORROSION CELLS

Corrosion cells can exist on the surface of a single metal. Anodic (corrosion) behaviour can be stimulated by many factors, some of which are in the metal itself such as residual stresses, included impurities, grain boundary segregation of alloying metals, and screw dislocations on crystal surfaces to mention a few. Oxygen availability at a surface ennobles the surface and creates a site for cathodic reactions which stimulate anodic reactions at nearby sites. This type of cell, called an oxygen concentration cell, is very important being one of the most common causes of the corrosion of buried steel. Oxygen concentration cells are also responsible for most attack in crevices and for non occluded pitting attack. Corrosion products on the surface of buried or immersed metal have a passivating effect and such a surface will act as a cathode when combined with new or freshly abraded metallic surfaces. Anodes sometimes corrode themselves into a sort of stagnation and can become cathodic to newly abraded surfaces. Anodic and cathodic reactions can occur at the same site or so close to one another the location of individual anodic and cathodic sites is very difficult. The cell potential referred to in the discussion of Gibb's Free Energy cannot be measured in the complicated world of underground and immersion corrosion. The corrosion potentials measured are therefore mixed potentials and can be visualized graphically using idealized polarization diagrams referred to in the literature as Evans' Diagram⁽⁵⁾. A typical Evans' Diagram is shown in Figure 12 below.

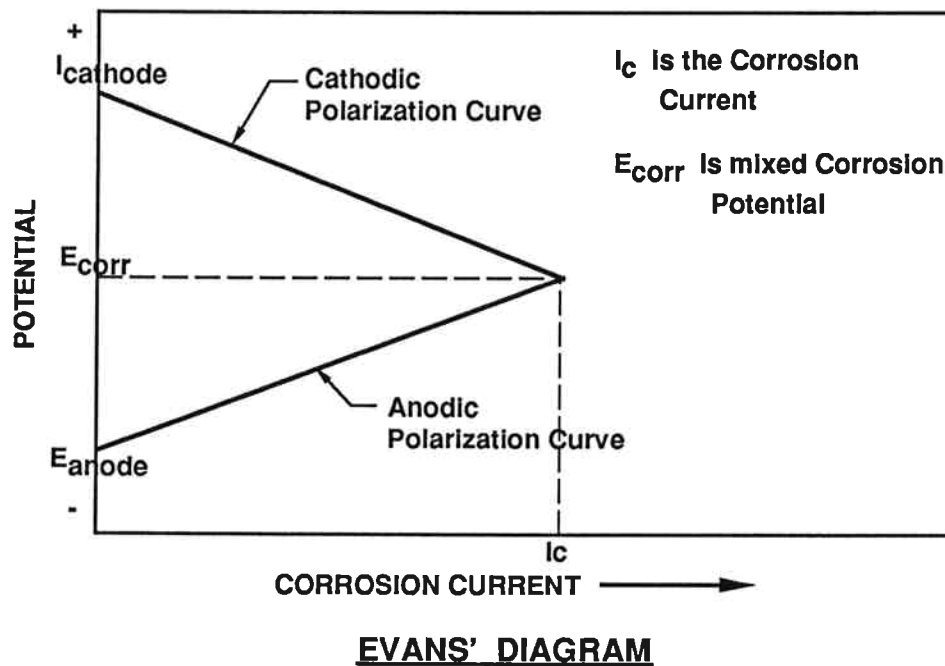


FIGURE 12

These diagrams although not experimentally derived are very useful in explaining many corrosion situations. Increasing activation and concentration polarization change the slopes of either the cathodic or anodic curves resulting in reduced corrosion current. The steepest curve controls the reaction rate as shown in Figure 13.

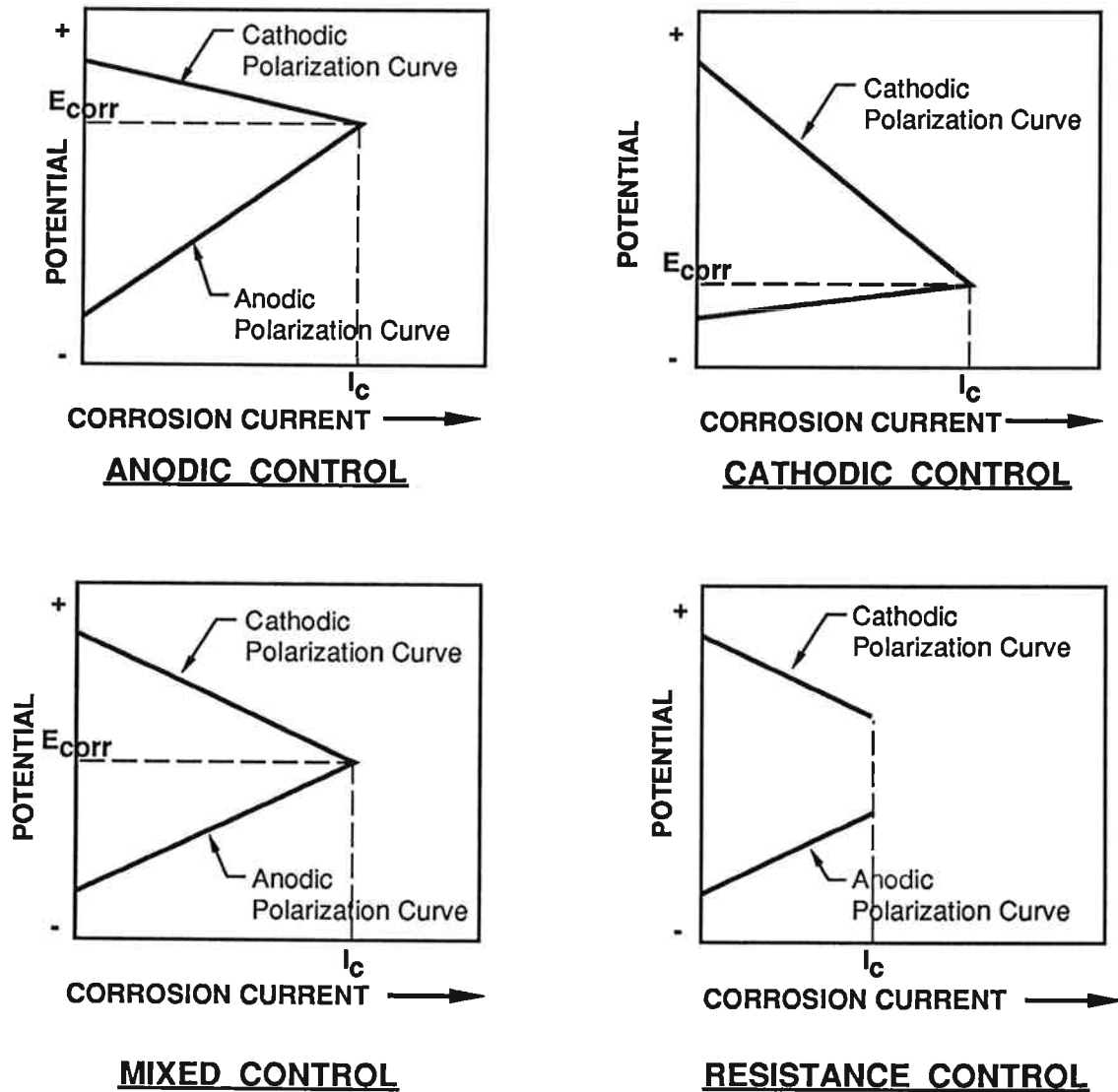


FIGURE 13

Assuming that the external metallic path is an excellent conductor, the resistance shown on the diagram is due to that encountered in the bulk electrolyte. The Evans' diagrams also are useful in describing the application of cathodic protection. If the definition of cathodic protection is "the polarization of the cathodes to the open circuit potential of the anode", then it can be shown diagrammatically in Figure 14.

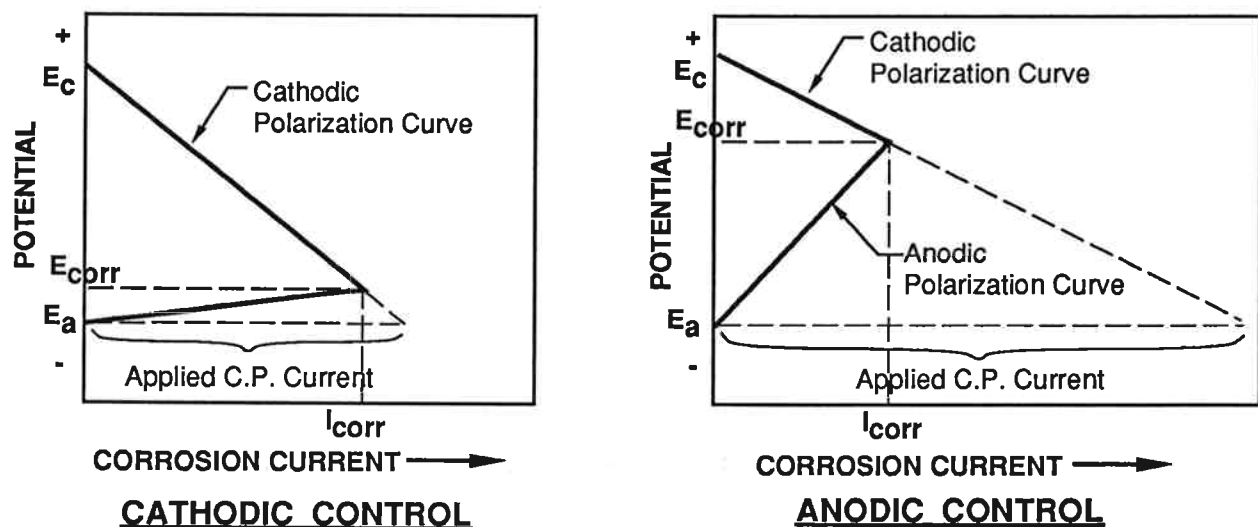


FIGURE 14

The diagrams show the difficulty of applying cathodic protection effectively when the corrosion process is under anodic control. Fortunately corrosion in neutral soils and seawater is under cathodic control, the polarization at the cathode being under the influence of oxygen diffusion.

Actual polarization curves are produced by adding or subtracting increments of current to or from a corroding system and recording the change of potential after stability is reached. The effects of this procedure are shown in Figure 15.

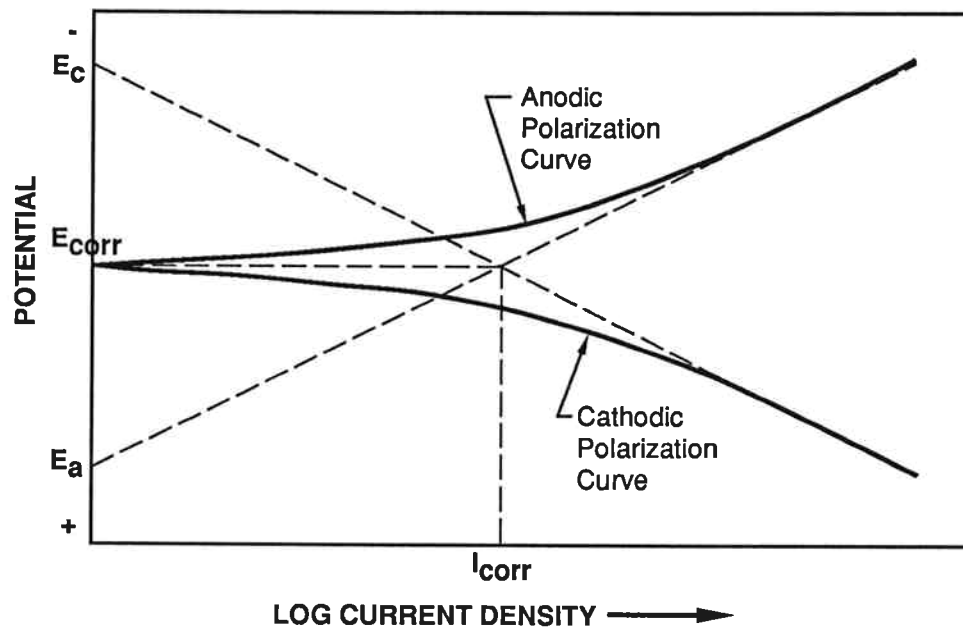


FIGURE 15

Extrapolation back from near linear portions cathodic and anodic polarization curves produce intercepts on the ordinate that are an approximation of the open circuit potential of the anodes and cathodes. A line drawn from the intersection of these extrapolations to the abscissa approximates the corrosion current for this system. It usually proves practically impossible to achieve a straight portion of the cathodic polarization curve since oxygen depletion occurs at high cathode current densities and no cathodic reaction can proceed until the potential is reached at which water dissociates. Once water dissociates the cathodic reaction becomes $2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2 \uparrow$.

CORROSION CURRENT AND METAL LOSS

In a corrosion cell consisting of anodes and cathodes on a single metal surface, it is not possible to measure the corrosion currents involved. The average corrosion current on small specimens

can be calculated from weight loss measurements using an assumption concerning the valence change of the corroding metal, Faraday's Equivalent, and the length of time the specimen was exposed to the corrodent. In cases where a galvanic cell is used to produce a useful electrical output, the life of the anode can be predicted if the product of the current output and time is known. If the electrical load is constant, then an instantaneous current reading will suffice to establish an approximate life of the anode material. Assumptions are made regarding the likelihood of changes in cell driving voltage and the possibility of serious local cell activity on the anode itself resulting in self-corrosion.

In general, if the current output of a galvanic cell is not resistance limited, the ratio of self-corrosion to useful cell output becomes small enough to be ignored. In some corrosion situations, stray current outputs can dominate the corrosion process. These currents originate, in many cases, from the operation of traction systems utilizing DC power. It is possible to measure the magnitude of these currents and to delineate the discrete areas at which discharge occurs. Again, assumptions have to be made concerning the anode process and the total coulombic discharge in any interval of time. This information and the use of Faraday's Equivalent will permit the calculation of anticipated metal loss.

If the corrosion process is denoted by $M^0 \rightarrow M^{2+} + 2e$ which is the expected anode oxidation reaction for iron or magnesium, then the equivalent mass of each of these metals is equal to their gram atomic mass divided by 2. In the case of iron, this becomes 27.9 grams and in the case of magnesium becomes 12.15 grams. If 1 ampere of current flowing in the corrosion circuit for 1 second results in the transfer of one coulomb of charge, then in one year the amount of charge transferred is over 31,500,000 coulombs. If this number is divided by Faraday's Equivalent and multiplied by 27.9 (equivalent mass of iron) it can be deduced that over 9,000 grams of iron has gone into solution. This figure is often stated as a dissolution rate of "20 pounds per ampere-year".

A similar calculation for magnesium yields a figure of 3,970 grams of metal dissolved by the passage of 1 ampere of current for a year. This amounts to about 8.7 pounds per ampere-year. Experience has shown that about twice this amount of metal actually dissolves, hence either the assumption that a bi-valent oxidation process is incorrect or self-corrosion of the anode material accounts for this discrepancy. It is also possible that both a univalent corrosion process and self-corrosion is responsible for the observed excess weight loss. Since magnesium does not react univalently, the discrepancy is assumed to be due to self-corrosion of the anode. Some metals exhibit the ability to corrode with several valencies, depending upon conditions in the electrolyte. In addition, species in solution can be oxidized at the anode, hence the assumption of the correct anode reaction or reactions is not always easy.

REFERENCES

- (1) Valency and Molecular Structure
Cartwell & Fowler, Butterworths, London, 1961

BIBLIOGRAPHY

Handbooks:

Corrosion, Vol. 1 & 2, L.L. Shrier
Newnes - Butterworths, London, 1976

Corrosion Handbook, H.H. Uhlig
John Wiley & Sons, New York, 1948

Corrosion Engineering, Fontana & Green
McGraw Hill, New York, 1978

Corrosion & Corrosion Control, Uhlig & Revie
John Wiley, New York, 1985

Corrosion and Its Control, Atkinson & Van Droffelaar
N.A.C.E., 1982