

Linear Polarization Resistance Monitoring

(LPR) Introduction

The electrochemical technique, commonly referred to as Linear Polarization Resistance, is the only corrosion monitoring method that allows corrosion rates to be measured directly, in real time. Although limited to electrolytically conducting liquids, the response time and data quality of this technique make it clearly superior, where applicable, to all other forms of corrosion monitoring.

Linear polarization resistance is particularly useful as a method to rapidly identify corrosion upsets and initiate remedial action, thereby prolonging plant life and minimizing unscheduled downtime. The technique is utilized to maximum effect when installed as a continuous monitoring system.

This technique has been used successfully for over thirty years, in almost all types of water-based, corrosive environments. Some of the more common applications are:

- Cooling water systems
- Secondary recovery system
- Potable water treatment and distribution systems
- Amine sweetening
- Waste water treatment systems
- Pickling and mineral extraction processes
- Pulp and paper manufacturing
- Hydrocarbon production with free water

Principle of Measurement

When a metal/alloy electrode is immersed in an electrolytically conducting liquid of sufficient oxidizing power, it will corrode by an electrochemical mechanism. This process involves two simultaneous complementary reactions.

At anodic sites, metal will pass from the solid surface into the adjacent solution and, in so doing, leave a surplus of electrons at the metal surface. The excess electrons will flow to nearby sites, designated cathodic sites, at which they will be consumed by oxidizing species from the corrosive liquid. A simple example of iron dissolving in acidic solution is illustrated in Figure 1.

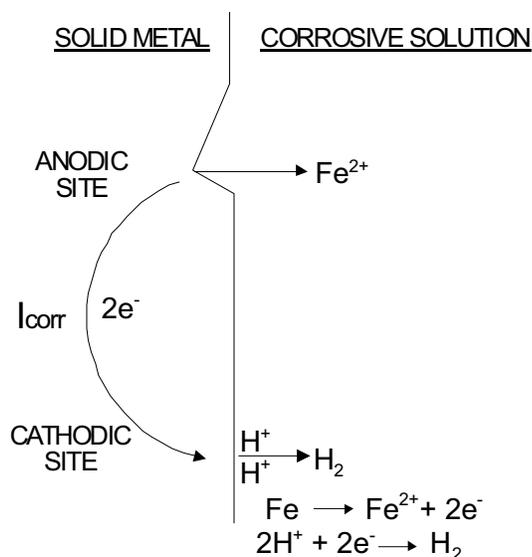


Figure 1.

The corrosion current (I_{CORR}), generated by the flow of electrons from anodic to cathodic sites, could be used to compute the corrosion rate by the application of a modified version of Faraday's Law:

$$C = \frac{I_{CORR} \times E}{A \times D} \times 128.67 \quad (1)$$

where:

- C = Corrosion rate in "mils per year" (MPY)
- E = Equivalent weight of the corroding metal (g)
- A = Area of corroding electrode (cm²)
- d = Density of corroding metal (g/cm³)

However, anodic and cathodic sites continually shift position, and they exist within a continuously conductive surface, making direct measurement of I_{CORR} impossible. Small, externally-imposed, potential shifts (ΔE) will produce measurable current flow (ΔI) at the corroding electrode.

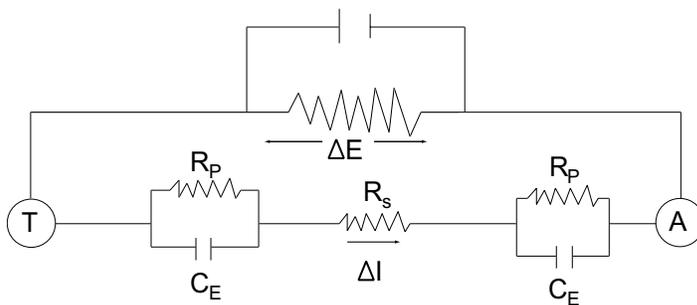
The behavior of the externally imposed current is governed, as is that of I_{CORR} , by the degree of difficulty with which the anodic and cathodic corrosion processes take place. The greater the difficulty, the smaller the value of I_{CORR} , and the smaller the value of ΔI for a given potential shift. In fact, at small values of ΔE , ΔI is directly proportional to I_{CORR} , and hence to the corrosion rate. This relationship is embodied in the theoretically derived Stern-Geary equation:

$$\Delta E / \Delta I = \frac{ba \ bc}{2.3 I_{CORR} (ba + bc)} \quad (2)$$

The numbers ba and bc are empirical rate constants, the Tafel constants, so the relationship can be more simply expressed as:

$$I_{CORR} = \Delta I / \Delta E \times constant \quad (3)$$

The value $\Delta E / \Delta I$ is known as the Polarization Resistance. In principle it is most easily measured by placing a second electrode (auxiliary) in the liquid, and connecting it to the corroding electrode (test) through an external power supply. This is illustrated in Figure 2.



- R_p = Polarization Resistance
- R_s = Solution Resistance
- C_E = Electrode Capacitance

Figure 2.

The applied potential, in this simple type of two-electrode measurement, is required to overcome the solution resistance as well as the polarization resistance of the corrosion reactions. Consequently, the polarization resistance will be overestimated by $\Delta I(R_s)$, and the corrosion rate will be underestimated to an extent given by:

$$C_M = \frac{C_A 2R_p}{2R_p + \Delta I(R_s)} \quad (4)$$

where:

C_M = Measured corrosion rate
 C_A = True corrosion rate

Metal Samples has largely overcome the problem of solution resistance error by using a three-electrode measurement (the PAIR™ technique). This uses separate circuits for the measurement of ΔI and ΔE . The circuit in which the ΔE measurement is made has an extremely high input impedance, consequently solution resistance has negligible effect on the value of potential shift applied to the test electrode. The basis of the PAIR™ technique is illustrated in Figure 3.

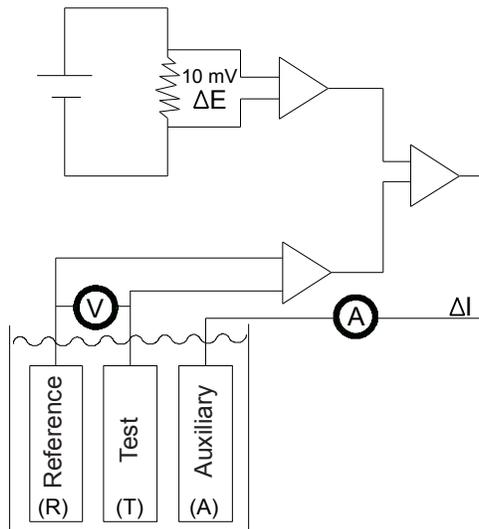


Figure 3.

PAIR™ is a trademark of Metal Samples.

When a measurement is made, the PAIR™ instrument will initially null any residual potential difference between the reference electrode (R) and the test electrode (T). After which, current will flow from the auxiliary electrode (A) onto the test electrode. The flow of current, between the auxiliary electrode and the test electrode, will increase until the test electrode potential is shifted 10 mV with respect to the reference electrode. The current (ΔI) required to sustain the 10 mV potential shift is proportional to the corrosion rate of the test electrode.

The polarizing voltage of 10 mV, that is used in PAIR™ instrumentation, has been chosen as being well within the limits for which the linear relationship between I_{CORR} and $\Delta E/\Delta I$ holds. Additionally, the value is sufficiently small as to cause no significant, or permanent disruption of the corrosion process, so that subsequent measurements remain valid.

The instrument reading is given directly as “mils per year.” The constant of proportionality, incorporated into the PAIR™ instrumentation, is an empirical number determined by comparison of $\Delta E/\Delta I$ values with weight loss measurements for several hundred alloy/environment systems. This ensures a sound, experimental basis for instrument calibration.

Individual corrosion rate measurements will show a decay characteristic, due to capacitive effects, that exist, to some degree, at all corroding electrode surfaces. This decay pattern is illustrated in Figure 4.

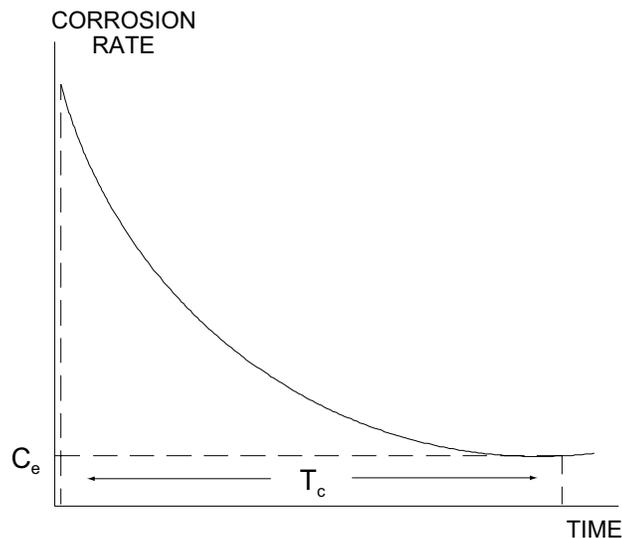


Figure 4.

The true value of corrosion rate is the equilibrium value (C_e) that is established after a time interval T_c . This time lag will vary, depending on the specific characteristics of the metal/environment system, between approximately 30 seconds and several hours. Since the decay characteristic is asymptotic, even systems with extreme “capacitive inertia” will closely approach equilibrium within 15-20 minutes; so that most practical measurements can be concluded within a 0.5-20 minute duration. A variable “time cycle” feature is incorporated into most PAIR™ instrumentation to accommodate this capacitive time-lag.

Probe Electrode Selection

Three-electrode probes are available with a triangular or linear-pin configuration, and in a concentric-ring, flush arrangement. When solution resistances reach extremely high values ($10\text{k}\Omega/\text{cm}$), the choice of electrode configuration becomes important. This is due to the spreading effect produced by high resistivity on the current field between the test and auxiliary electrode that, at some point, will allow current to impinge on the reference electrode and displace its potential. The effect is illustrated in Figure 5.

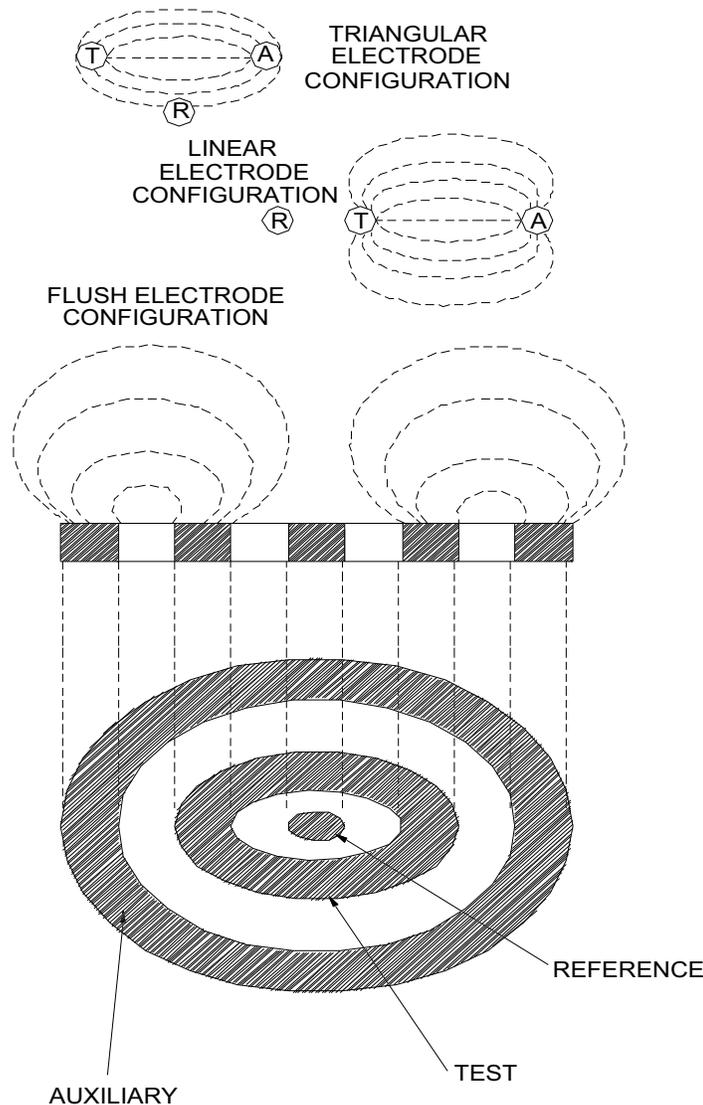


Figure 5.

Clearly, a linear-pin electrode configuration is less effected by “current spread” than is a triangular array. Concentric ring, flush, electrode configurations are essentially immune from “current spread” effects, due to mutual interference of current fields on opposite quadrants of the disc. As an approximate guide, a triangular electrode array can be used in solutions having specific resistances up to $10\text{k}\Omega/\text{cm}$, and the linear configuration up to $50\text{k}\Omega/\text{cm}$. In principle, the flush array will operate successfully as long as the environment offers some electrolytic conductance, however, $500\text{k}\Omega/\text{cm}$ is a good guide to practical working limits. Electrode configuration is, therefore, of primary importance in selecting a probe type for a given application.

Most other criteria for probe selection relate to the physical characteristics of the system, such as temperature and pressure ratings, and whether probe insertion/removal must be undertaken without system depressurization. Metal Samples offers a wide variety of probe body styles, addressing these various needs. The simplest probe body style is the fixed length version, an example of which is shown in Figure 6.

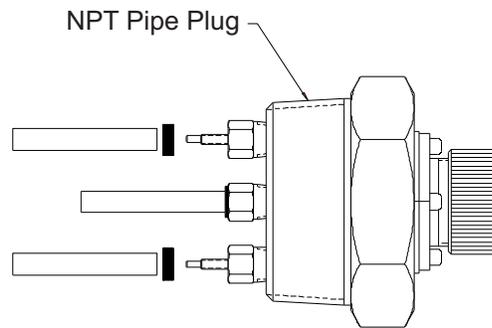


Figure 6. Fixed Length PAIR™ Probe

Typically equipped with an NPT bushing, the fixed PAIR™ probe is screwed into place. Probe installation requires system depressurization, unless an isolatable side-stream device is employed. Versions of this probe with 1" NPT, 1½" NPT, and 2" NPT entry bushing are available, with a maximum operating pressure of 3600 psi. An adjustable length version (shown in Figure 7) is also available with a movable entry bushing that will operate up to 1500 psi.

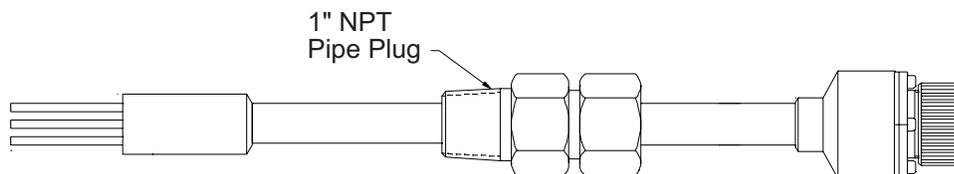


Figure 7. Adjustable Length PAIR™ Probe

Retractable probes, supplied with a 1" FNPT packing gland are available. Used in conjunction with a 1", full-port, ball-valve these probes can be inserted and removed without system depressurization at pressure up to 2000 psi.

Retractable probes can be supplied with a safety frame that prevents probe "backout" in high vibration systems, and aids the insertion/removal process at the high end of the pressure operating range (above 150 psi).

For insertion/removal at high operating pressures, Metal Samples offers the retrievable probe. This style probe can be inserted and removed, without system depressurization, at operating pressures up to 3600 psi. To accomplish high-pressure retrieval, the probe is used in conjunction with a special range of fittings, plugs, tools, and valves that are discussed in the High Pressure Access Fittings section of this catalog. The retrievable installation, a standard for the oil and gas production industries, is illustrated in Figure 8.

All probe body configurations discussed are for industrial use, and are constructed of AISI 316L stainless steel. As such, they meet NACE material standard MR0175 for sour service use. Additionally, all industrial quality PAIR™ probes have a glass-sealed, electrical connector that has an operating pressure rating of 6000 psi, to provide a "backup" seal in the unlikely event that the primary electrode seals fail.

Metal Samples also offers a range of laboratory PAIR™ probes and cells, side-stream devices, custom test-loops for laboratory investigation.

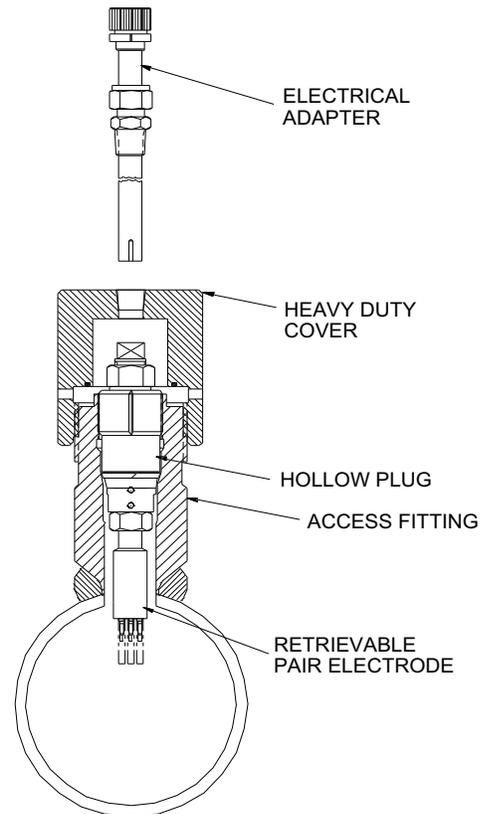


Figure 8.

Instrumentation

Metal Samples offers a wide range of PAIR™ instrumentation to suit almost any customer application. Instrument products offered include:

- Handheld Meters and Data Loggers
- Field-Mounted Data Loggers
- Field-Mounted Transmitters

Replacement Electrodes

Replacement of electrodes by the user is a convenient feature of Metal Samples probes. Field changes are quickly made without special tools or techniques.

Comparisons of metals and alloys under operating conditions can be conveniently and economically accomplished. Substitution of identical fresh electrodes of the same material for badly corroded or contaminated electrodes is a practical approach to evaluating changes in process conditions or inhibitor effectiveness from the same starting conditions of surface quality and dimensions.

The use of the replacement electrodes for weight loss measurements is an attractive possibility for many experimenters. The fact that both polarization and gravimetric measuring methods are made on the same test specimen eliminates several variables from comparative evaluations.

With the 3-electrode system, surface areas of the different metals and alloys are adjusted to compensate for variations in chemical activity and density. Thus a direct mpy meter readout is obtained in each case for the electrodes listed.

Electrodes are sold as a single unit. In most cases, the electrodes used will be of the same metal alloy; however, some users may wish to vary the electrodes. Each electrode is enclosed in an inhibited paper package along with a gasket. Viton® gaskets are standard and supplied unless another material is specifically requested.

Electrodes can be provided from many alloys with material supplied either by Metal Samples or by the customer. Electrodes from the customer's weld metal can be machined by Metal Samples. Inquiries for electrodes of special alloys are encouraged.

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