Anodic Protection—Its Operation and Applications

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Most metals will corrode within a certain range of electrical solution potential and solution pH. At potentials more negative than this range, corrosion ceases (cathodic protection). At potentials more positive than this range, several metals become passive. For these metals the potential can be shifted electropositively into the passive range through anodic protection (AP). AP is especially applicable to sulfuric acid (H_2SO_4) and caustic liquor environments. It often permits a designer to use a low alloy rather than a corrosion-resistant metal, at an overall cost saving.

Most metals exposed to a liquid-phase corrosive environment can be protected from aggressive corrosion attack using an electrochemical prevention technique—either cathodic protection (CP) or anodic protection (AP). Selecting the appropriate protection method depends primarily on the metal/environment characteristics.

Whether a metal can corrode in a particular environment can be determined thermodynamically. Figure 1[1] is a diagram for iron in an aqueous environment. It shows domains of immunity, corrosion, and passivity with relation to the iron electrical solution potential (E_H) and solution pH.

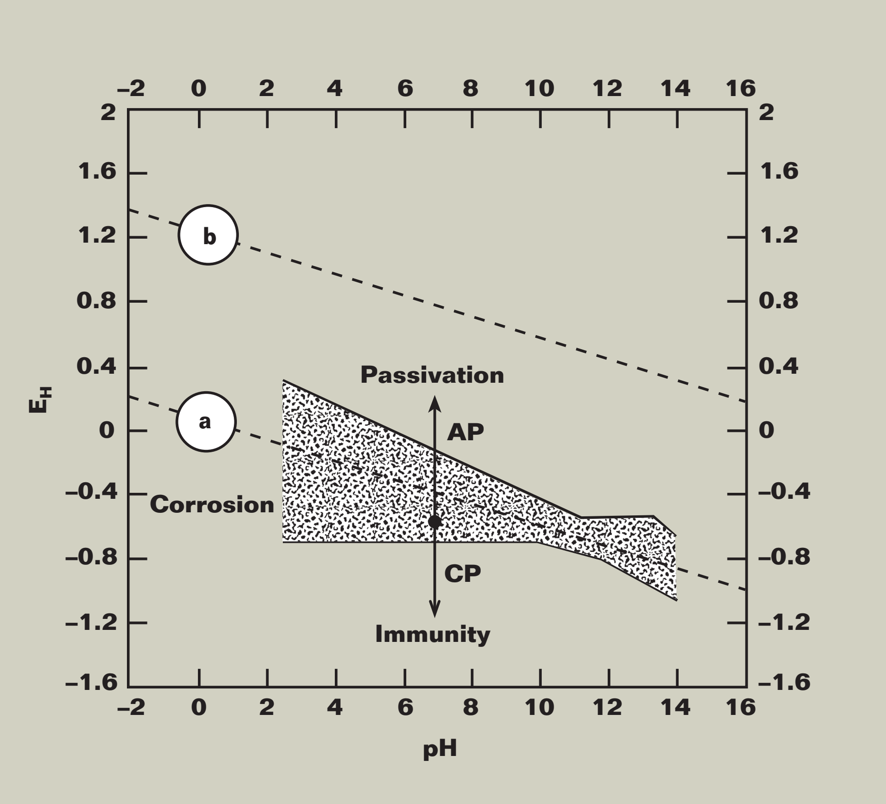
Although the thermodynamic calculations leading to the construction of this diagram can determine whether steel can corrode, they do not predict the rate of corrosion. In contrast, corrosion is thermodynamically impossible at a given pH if the steel/environment potential is maintained in the immunity zone (e.g., –0.80 V, pH 3 to 9). Accordingly, if a steel surface corrodes actively and its solution potential shifts electronegatively—as is the case with CP—then corrosion is preventable. Conversely, the corrosion potential of metals exhibiting active-passive behavior in some situations (e.g., steel, nickel, titanium, and stainless steels [SS]) can be shifted in the anodic (electropositive) direction to produce a passive surface and hence a large reduction in corrosion rate.

Theory of AP

A number of metals exhibit what is known as "active-passive" transition when polarized in the electropositive direction (Figure 2). In this state, the potential of a metal moves into a passive region when it shifts to the electropositive direction after direct current (DC) is applied. A passive surface film forms, resulting in a decrease in corrosion current density (CD) and hence a lower corrosion rate. Increasing anodic polarization into the transpassive range may cause a breakdown in the passive film and lead to pitting-type corrosion.

At greater than a critical current density, formation of the passive film is essentially a coulombic (total charge) effect; therefore, the amount of current required to pass the primary passive potential is a function of time (e.g., higher currents are required when the time period is short and vice versa). The current required to passivate the metal surface is usually an order of

FIGURE 1



E_H-pH diagram for iron in water.

magnitude greater than the current required to maintain passivation.

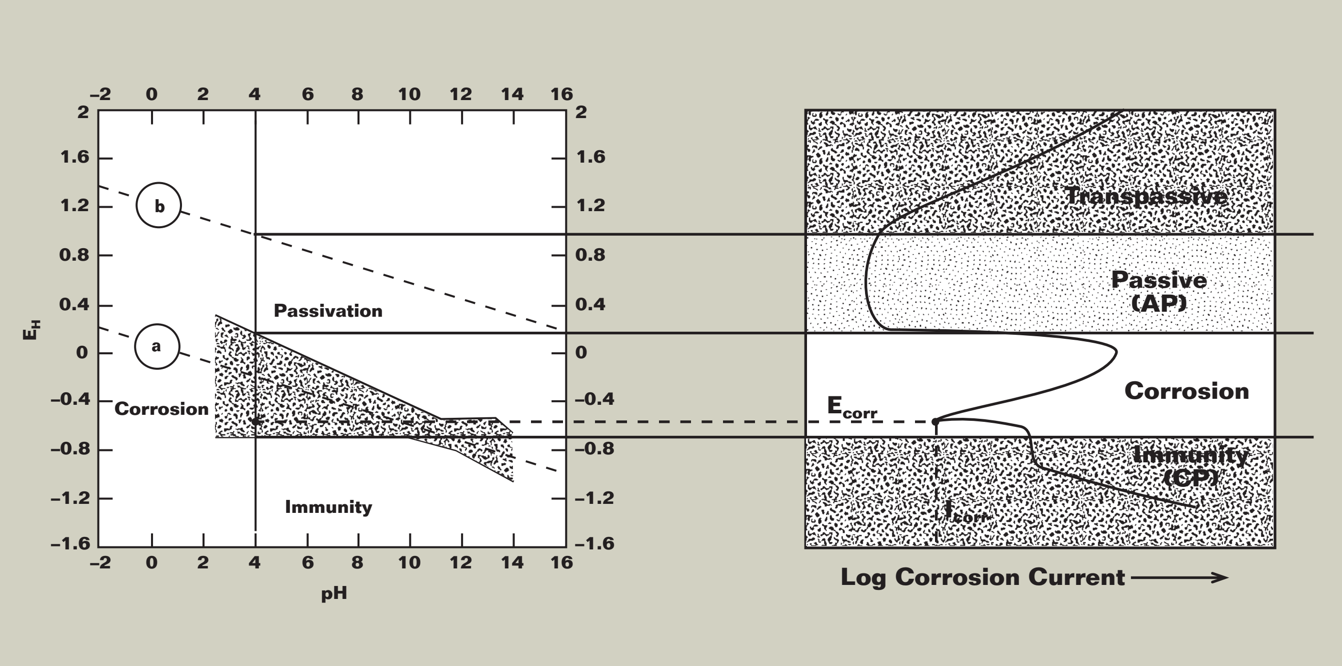
The passive potential range and the CD required to achieve passivation are functions of the type of metal and electrolyte and of factors such as pH, temperature, degree of oxidation, etc. Mild steel, SS, titanium, and many other metals in the transition group exhibit active-passive behavior.

Figure 3 shows a general AP schematic for a tank or vessel.

The AP current is supplied by a potential-controlled power supply that is necessary to maintain the structure at a fixed potential in the passive range. It is common to predetermine the ideal set potential for the operation either by laboratory testing or, more preferably, by running potentiostatic anodic polarization curves on coupons in the actual vessel.

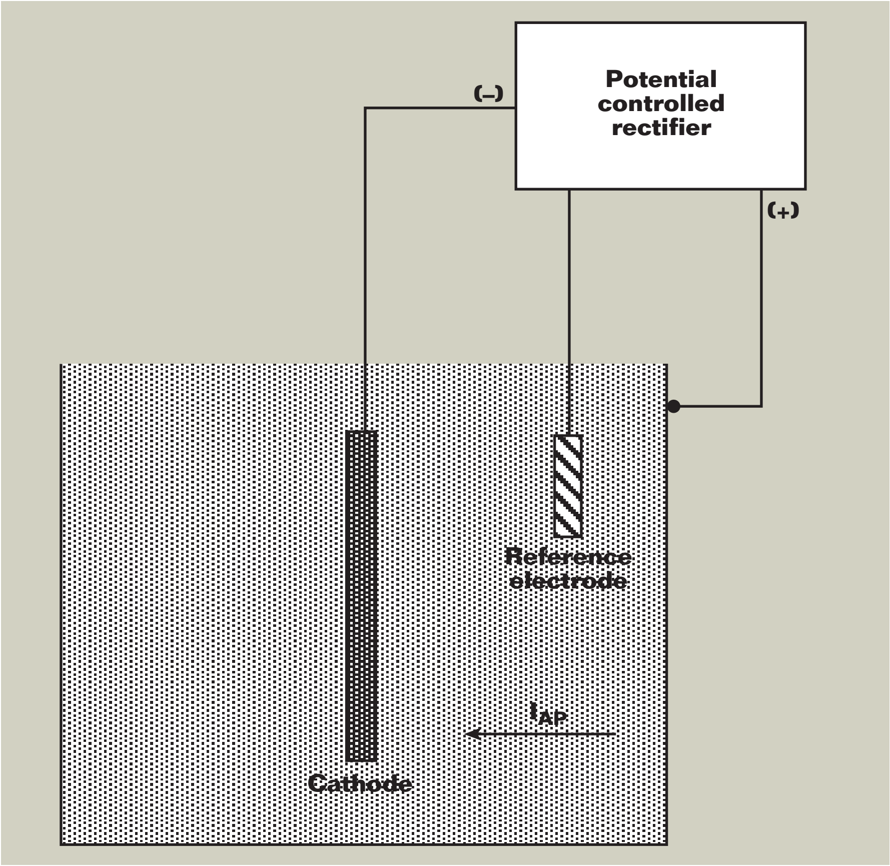
The reference electrode is necessary to provide a feedback potential measurement for comparison to the set potential. The type of reference electrode used depends on its compatibility with the liquid medium. Typical ref-

FIGURE 2



E_H-pH diagram in conjunction with an AP polarization curve.

FIGURE 3



Schematic of an AP system.

TABLE 1

CORROSION RATE OF 316 SS (mpy) IN H_2SO_4

	93% H_2SO_4		98% H_2SO_4	
Temperature	**Unprotected**	**Protected**	**Unprotected**	**Protected**
70°C	29	<2	—	—
100°C	495	25	41	<2

erence electrodes are platinum, calomel, silver/silver chloride (Ag/AgCl), mercury/mercury sulfate (Hg/$HgSO_4$), and SS.

Cathode materials are also chosen with respect to their durability in the liquid medium, particularly because the cathode often passes through the vapor zone and leaves it susceptible to aggressive atmospheric corrosion. Common cathode materials are steel, chromium-nickel steel, Hastelloy C†, and platinum clad brass.

AP is most often used to protect mild steel and SS sulfuric acid (H_2SO_4) storage tanks and, to a lesser extent, coolers and piping. It has also been applied to mild steel in certain fertilizer solutions. Any situation in which a metal/solution combination produces active-passive behavior is a potential candidate for AP if a corrosion problem arises.

H_2SO_4 Equipment

The corrosion rate of either steel or SS in H_2SO_4 service is a function of both temperature and acid concentration. Table 1[2] indicates the typical corrosion rate reduction that can occur on 316 SS in two concentrations of H_2SO_4 by the application of AP.

Figure 4[2] shows an anodic polarization curve for 316 SS (UNS S31600) in 93% H_2SO_4 at 70°C. Note that the CD required to achieve passivation is almost 10^4 µA/cm^2 (10 A/ft^2). This potentiodynamically derived polarization curve would indicate that an impractically large current capacity power supply would be required to exceed the active-passive transition point. Fortunately, smaller-capacity units are feasible when operated galvanostatically to take advantage of the coulombic effect. Current densities to maintain passivation are normally an order of magnitude lower than the primary transition current.

An interesting application of electrochemical protection involves the combined use of AP and CP for corrosion mitigation in acid coolers (Figure 5). The shell and tubes, made of 316L SS and exposed to the acid, are anodically protected where two Hastelloy rods, inserted in the place of two tubes, act as the cathodes. In addition, the carbon steel (CS) head boxes exposed to cooling water are protected with galvanic anodes. Piping carrying H_2SO_4 can also be protected anodically.

Alkaline Process Equipment

The use of AP in alkaline environments is almost entirely limited to the pulp and paper industry for the protection of pulp digesters and storage tanks handling caustic kraft liquors, which are a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S). CS can also be anodically protected in NaOH solutions at elevated temperatures.

Economic Considerations

AP can be installed in conjunction with new and existing structures. The economic benefits are attractive in both cases.

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†Trade name.

AP may allow the vessel designer to use a less expensive material or alternative corrosion mitigation technique. As an example, a tank used to store concentrated H_2SO_4 can be fabricated from CS with AP as opposed to more expensive SS or CS with an organic lining.

The cost effectiveness of AP is a function of vessel surface area. In general, protecting a larger vessel translates into a significantly reduced price per unit surface area.

Remote Monitoring

As a result of the large differences in corrosion rates between vessels in the active and passive state, it is imperative that AP systems operate correctly for as much time as possible. As such, virtually all systems are supplied with a remote monitoring unit (RMU).[3] This computer-based unit allows offsite experts to review, and analyze operational data and recommend changes.

Conclusions

AP electrochemical systems supply a process or maintenance engineer with powerful corrosion control tools that can be applied to equipment exposed to various liquid-phase environments, especially H_2SO_4 and caustic liquors. AP can be installed during construction or at a later date by retrofitting. These systems require external electrical power and must be operated continuously to be effective—this can sometimes be an added maintenance requirement. New remote monitoring technology, however, facilitates system supervision and allows for automatic status checks either by the process operator or the system supplier.

References

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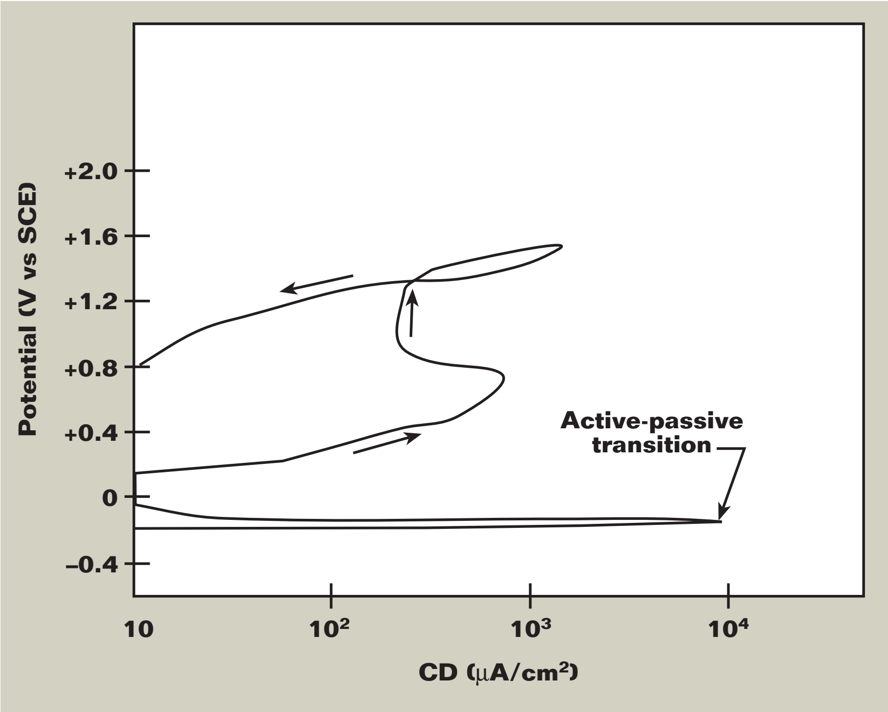
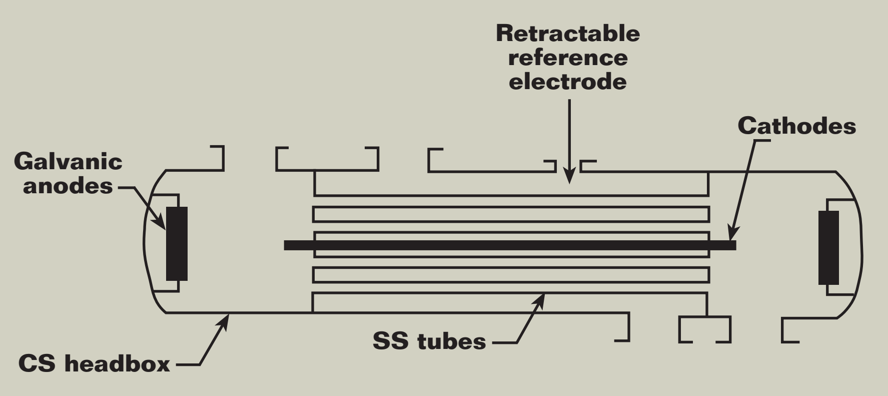
3. W.W. Shim, J.I. Munro, "Anodic Protection in the Sulfuric Acid Industry," MP 39, 12 (2000).

FIGURE 4



Polarization curve 316 SS in 93% H_2SO_4 at 70°C.

FIGURE 5



AP of acid coolers.

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