

# Anodic Protection in the Sulfuric Acid Industry

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**This article discusses the use of anodic protection (AP) in combating iron contamination, general tank wall wastage, and hydrogen grooving in carbon steel sulfuric acid ( $H_2SO_4$ ) storage tanks. It also addresses the use of AP for stainless steel acid piping and coolers. Topics include experiences using AP in acid storage tanks, theory of AP, design philosophy, engineering materials used, and remote monitoring equipment.**

Anodic protection (AP) is an electrochemical corrosion protection technique that can be applied to a variety of process vessels, including carbon steel (CS) tanks storing concentrated sulfuric acid ( $H_2SO_4$ ). AP should not be confused with the more traditionally used cathodic protection (CP) technique, which is generally used only in neutral pH environments. AP is applicable in alkaline and acid environments but can be used only in specific combinations of process chemistry and metals. Figure 1 shows different electrochemical corrosion protection techniques.

A significant benefit of AP is that  $H_2SO_4$  remains pure. At concentrations of 93 to 98%, the acid is not very corrosive to steel. The owner's main concern is contamination by corrosion products resulting in an inferior grade

of acid. The rate of iron contamination depends on factors such as temperature, acid strength, and the ratio of acid volume to surface area in contact with acid. Reported data indicate 10 to 19 ppm/day of iron pickup for acid at 94, 98, and 100% concentrations.<sup>1,3</sup>

Another concern of tank owners is hydrogen grooving of internal tank walls. The damage is more prevalent near the upper half of the manhole and nozzles. The hydrogen is a product of the reduction reaction that completes the corrosion process. AP prevents such damage.

Theoretically,  $H_2SO_4$  tanks can be protected by CP; however, such a CP system would be prohibitively expensive because of the large current requirement. Alternative methods of preserving acid purity include the use of stainless steel (SS) and fiberglass tanks. The economic feasibility of AP is a function of tank size. Systems installed on large tanks are very cost effective.

To ensure continuous and effective AP operation, a remote monitoring unit (RMU) is included as part of the installation. The RMU is connected to a standard telephone jack and 120-V alternating current (AC) service and can be remotely contacted to download the operating data from the system.

## Theory of AP

The theory of AP is well documented elsewhere.<sup>4,5</sup> The essential condition for using AP is that the metal must exhibit an active/passive behavior in the environment of interest. Figure 2 depicts a polarization curve of an active/passive metal environment combination. The vertical axis is the electrochemical potential and the horizontal axis is the current applied to the tank. The electrochemical potential is a voltage reading taken with a reference such as the saturated calomel electrode (SCE) (Figure 3). By using an external direct current (DC) source and auxiliary cathodes, the potential of the tank can be moved into the passive region.

At this potential, the corrosion rate is reduced several orders of magnitude.

The passivity of steel in  $H_2SO_4$  is a phenomenon that allows corrosion products to build up a fairly impervious and tenacious physical barrier on the surface of the steel. The thickness of this barrier is measured in nanometers, but it possesses the characteristics necessary to prevent further metal corrosion. "Electrochemical coating at the atomic scale" is a fairly accurate description of this phenomenon.

## AP Hardware

The basic AP hardware consists of a DC current source, auxiliary cathodes, reference electrodes, and signal conditioning electronics. The reference electrode senses the electrochemical potential of the tank and provides feedback to the potential control current source. The electronics control the precise amount of current required to maintain the tank in the passive region. The cathodes are used to complete the external DC circuit. Figure 4 indicates the basic layout of an AP system. Figure 5 shows the components in detail.

The first AP system in  $H_2SO_4$  dates from the 1950s. Over the years, a number of improvements in system design have been undertaken. Several of these are described below.

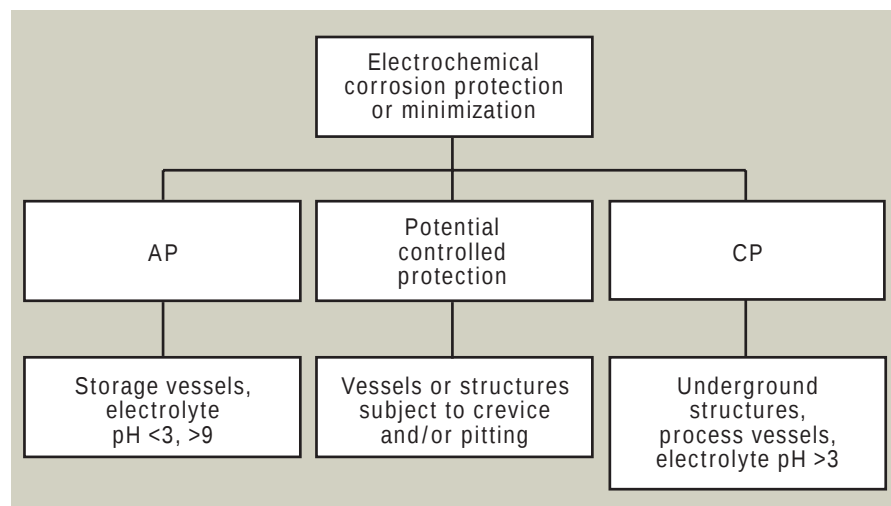
### CURRENT SOURCE

The DC current can operate single or three-phase AC power. A NEMA 4X enclosure is used to protect the current source from the harsh plant atmosphere. Recently, systems were installed with a distributed current source. This separates the power source from the control electronics to minimize the size and cost of high-current wiring.

### CATHODES

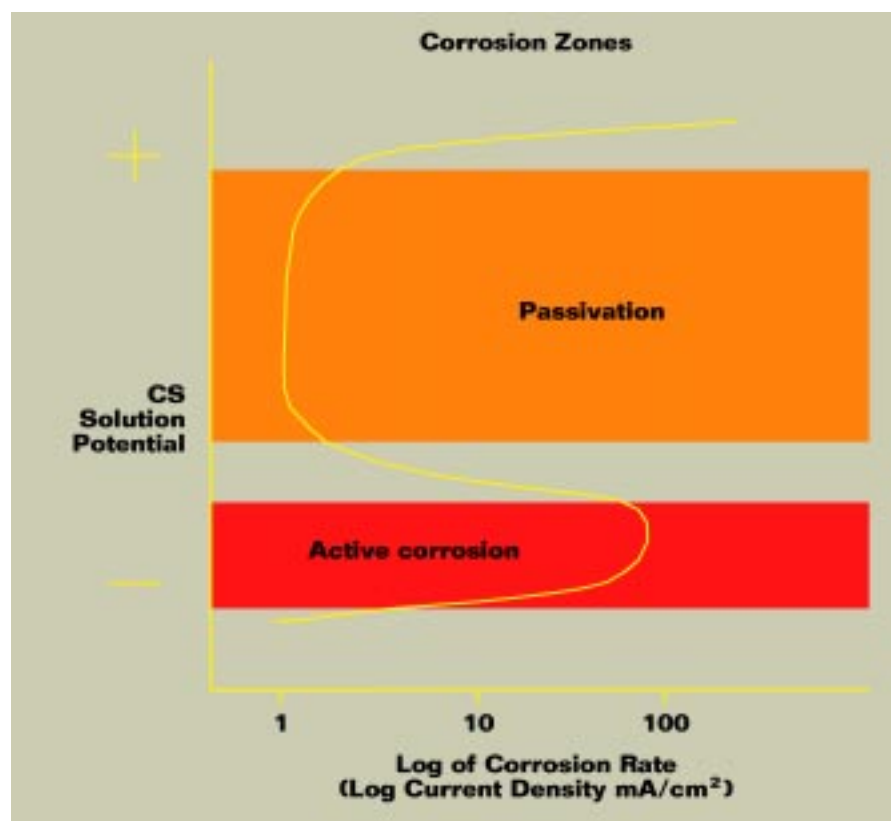
In the past, austenitic SS pipes were used as cathodes. However, this practice has been abandoned because of possible hydrogen embrittlement of

**FIGURE 1**



Regimes of electrochemical protection techniques.

**FIGURE 2**



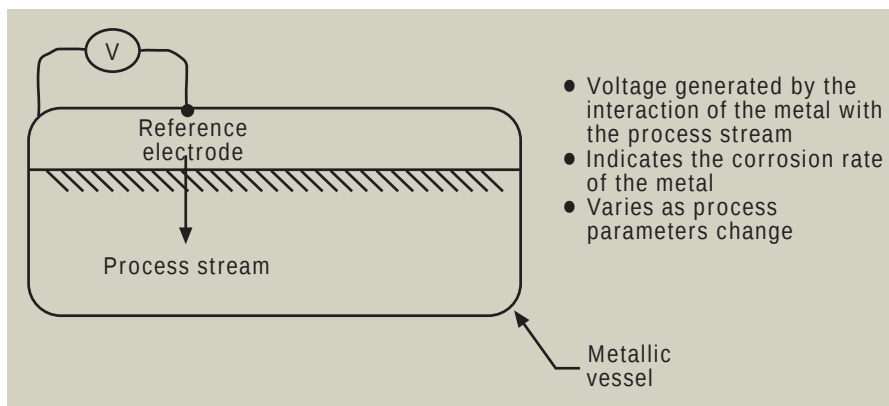
Polarization curve showing active/passive behavior.

the cathodes. Present cathodes are lightweight, small-diameter, and fairly flexible. Typical materials used are steel, chromium-nickel steel, Hastelloy

C,<sup>†</sup> and platinum-clad brass. Proprietary composite materials with good corro-

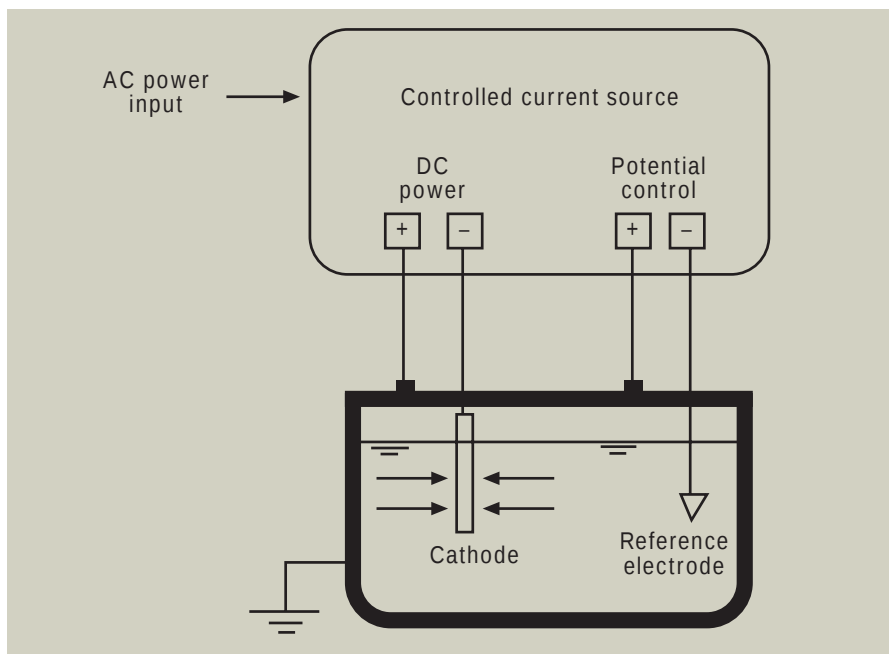
<sup>†</sup>Trade name.

FIGURE 3



Solution potential measurement.

FIGURE 4



Basic AP system.

sion resistance and current-conducting properties are also used.

## SPARK PREVENTION

A concern of using AP in  $H_2SO_4$  is the possibility of sparks if the acid level drops below the ends of the cathodes. Sparks are not acceptable since the tank may contain significant concentrations of hydrogen gas caused by the corrosion process or use of AP.

AP systems are designed with two safety features to prevent sparking.

First, the system is interlocked with the electronic tank level equipment so as to de-energize the AP at low acid levels. Second, a patented fiber braid assembly is also used around each cathode to prevent sparking. These two safety measures are normally used concurrently.

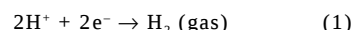
## Iron Contamination

Table 1 indicates data showing the effectiveness of AP in reducing iron pickup in storage tanks. Prior to using

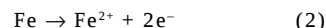
an AP system, the iron content measured as high as 160 ppm. Although the data are spotty, they illustrate that the iron content in both tanks was reduced to a fraction of the original value after the AP system was energized in April 1993.

## Hydrogen Grooving

Many acid tanks exhibit hydrogen grooving caused by the reduction of hydrogen ions in the acid to hydrogen gas (cathodic reaction):



where the complementary reaction is the oxidation of steel that may be written as:



This is commonly observed in the manhole area. Typically, the grooving concentrates on the wall near the upper half of the manhole area. The damage occurs as a result of hydrogen gas forming and streaming up the manhole, disrupting the loose iron sulfate ( $FeSO_4 \cdot 7H_2O$ ) passive film.<sup>4</sup> This grooving can cause localized corrosion allowance consumption fairly rapidly. AP mitigates the iron dissolution, consequently stifling the cathodic reaction of hydrogen gas formation and preventing this type of damage.

## Anodic Protection of Acid Coolers and Piping

$H_2SO_4$  coolers and piping are generally made of austenitic SS such as type 316 (UNS S31600). The concentration is normally 93 to 98% acid and oleum. AP provides the benefit of preventing through-wall pitting that results in equipment failure, personnel hazard, and environmental impact caused by spillage.

At room temperature, SS coolers and piping are immune to attack by 93 to 98%  $H_2SO_4$ . As the temperature increases, however, the electrochemical potential begins to fluctuate between active and passive behavior.

This fluctuation becomes easily observable, and it becomes distinct at ~75°C and higher.<sup>6</sup> As the temperature increases, the fluctuations increase in frequency. Eventually, the SS will remain active. AP is useful in this case in restricting this fluctuation. By imposing a positive current that maintains the potential in the passive region, the life of the SS can be increased by orders of magnitude.

The current required to maintain passivity on SS is not very large. It is imperative that the potential is not forced into the transpassive zone (Figure 2) because the corrosion rate can be increased. The key here is a reliable reference electrode that will give a good feedback signal. The reference electrode has to be stable, reproducible, and capable of withstanding the operating temperature and pressure of the acid environment.

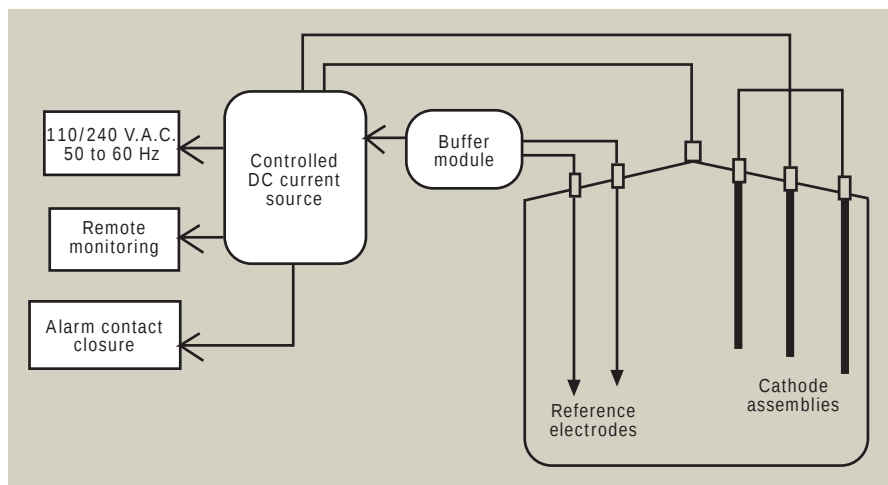
In the case of acid piping, the spacing of cathodes is critical. Too few cathodes result in a current distribution problem. Too many cathodes render the project economically unfeasible in terms of both materials and installation. In general, cathode spacing is a function of pipe diameter. The larger the piping, the larger the cathode spacing. Normally, AP is not cost-effective for piping <6 in. (152 mm) in diameter.

Erosion of the AP cathode occurs with coolers and piping but not with storage tanks. The high-velocity acid erodes the cathode surface. This requires periodic replacement of the cathode. As a result, on-site replacement must be designed into the protection system.

## Remote Monitoring

Although the AP system is an important piece of equipment in the plant, it is not the primary focus of plant personnel. It is important, therefore, to monitor the AP system without being intrusive or adding an extra burden to the plant operators and personnel. The RMU was developed to fulfill this need.

**FIGURE 5**



AP block diagram.

**TABLE 1**

## EFFECT OF AP IN LOWERING IRON CONTAMINATION OF H<sub>2</sub>SO<sub>4</sub> DURING STORAGE

| Date     | Truck (ppm of iron) | Tank 1 (ppm of iron) | Tank 2 (ppm of iron) |
|----------|---------------------|----------------------|----------------------|
| 10/6/92  | 57                  | 3                    | 32                   |
| 10/27/92 | 91                  | —                    | —                    |
| 1/11/93  | —                   | 49                   | 160                  |
| 3/15/93  | —                   | 21                   | 41                   |
| 4/12/93  | —                   | 37                   | 56                   |
| 4/14/93  | A/P online          | —                    | —                    |
| 4/19/93  | —                   | 19                   | 40                   |
| 4/21/93  | 19                  | —                    | —                    |
| 4/22/93  | 19                  | —                    | —                    |
| 5/3/93   | —                   | 6                    | 6                    |

<sup>(A)</sup>AP system was energized on 4/14/93. The truck delivered the acid to Tank 1 and Tank 2.

The RMU is a microprocessor-based computer complete with a modem. It can monitor the operating parameters of AP systems remotely via a voice-grade telephone line. The unit has built-in memory to store an average of 10 days' operating data. Normally, after 7 days, the RMU is called and the data are downloaded and plotted.

Typical recording channels are DC current, DC voltage, all reference electrode potentials, and temperature of current source. In addition, the plant may provide an analog signal from the acid level sensor.

With simple hardware additions, the RMU is capable of turning systems on and off and changing set points remotely. Other control schemes are possible, and plans for future upgrades are in progress.

## Other AP Applications

In general, any active/passive metal environment combination may be a candidate for AP. Laboratory study followed by field coupon trials can determine whether an AP system is an effective method of controlling and preventing corrosion.

## Conclusions

AP is a powerful tool to combat iron contamination of strong  $H_2SO_4$ . For large tanks, this is a very cost-effective solution.

An RMU may be used to monitor the operating parameters of AP systems as well as any other plant operating parameters. The RMU may also be used to control operating systems.

Numerous other industrial applications for AP have yet to be explored. Laboratory study followed by field coupon trials will uncover the data necessary to evaluate the effectiveness of AP.

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