

How anodic protection halts corrosion

New techniques may allow cheaper steels to be used in severely corroding environments. Here's how anodic protection works. By H. A. Webster

Recent work has made possible the application of anodic protection techniques to metals in active chemical environments. One outcome of this research is strong evidence to suggest that mild carbon steel and low-alloy stainless steel can be rendered

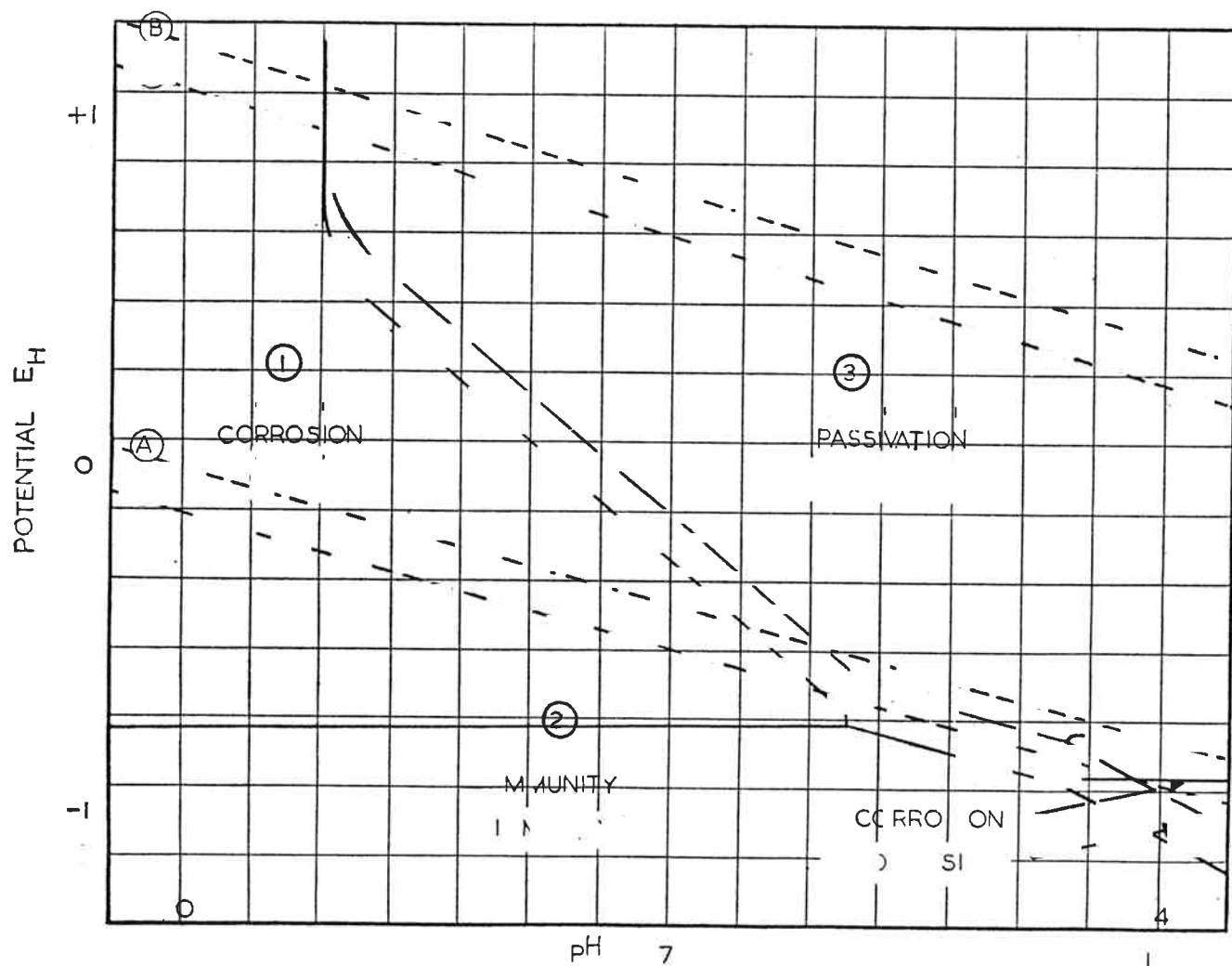
almost inert to severely corroding environments.

The concept of cathodic protection is now generally understood by the majority of engineers involved in the design and operation of chemical plants. In essence, cathodic protection

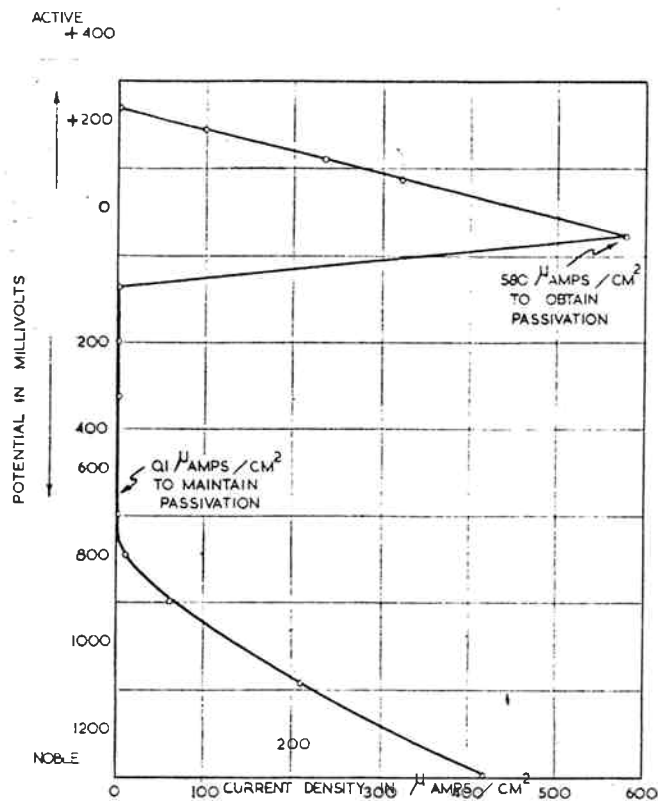
consists of making a corroding surface sufficiently negative with respect to its environment so that metal ions cannot leave its surface.

Sometimes this phenomenon is equated to the phenomenon of passivation, but it should be more correctly called a phenomenon of immunity, the term passivation being reserved for electrode conditions in which the surface is covered by a very thin adherent passive layer.

Passivity is responsible for the corrosion resistance of aluminum and

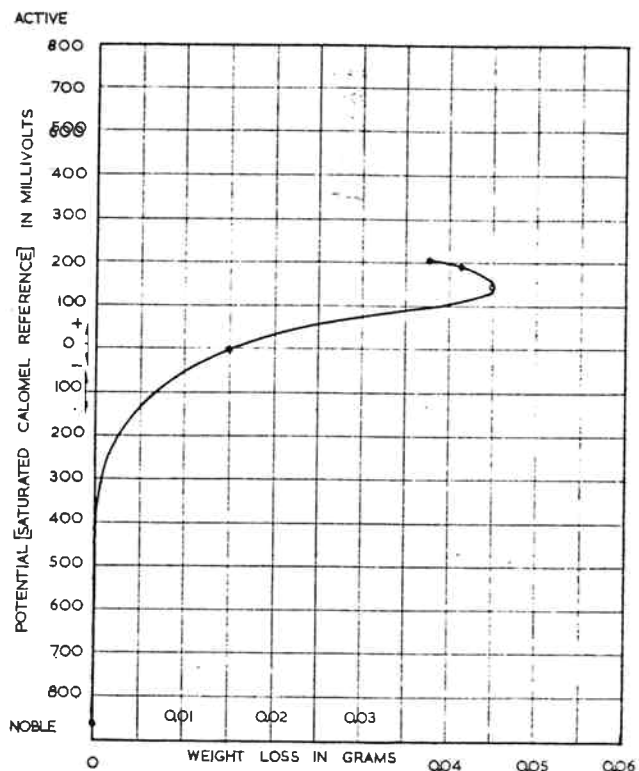


Pourbaix diagram outlines condition of metal surface in contact with solutions of varying pH. Fig. 1



Polarization curve for 316 ss in 67% acid. Fig.

2



Metal loss for 316 ss in 67% sulfuric acid. Fig.

3

stainless steels, since they rely upon these surface layers for their superior performance in chemical environments. Where these materials do not perform satisfactorily, it can usually be demonstrated that the environment attacks the protective oxide layer directly, rendering the material active.

Defining the limits of corrosion

Dr. M. Pourbaix, director of Belgian Corrosion Research Centre, has investigated the relationship between electrode potentials and corrosion activity for various systems. He plotted electrode potential against pH to produce equilibrium diagrams which clearly demonstrate the potentials at which we would expect immunity, corrosion, and passivation.

He established boundary areas by arbitrarily relating these boundaries to the solubility of iron in the solution. He postulated that iron was corrodible (or not corrodible) in an iron-free solution according to whether the solubility of iron in this solution is higher (or lower) than a very small value which he designated to be

10^{-6} gram-ions per litre (0.056 milligrams/litre).

The lines corresponding to that solubility divided the electrode potential — pH diagram into several areas (see Figure 1):

Area No. 1, or area of corrosion within which corrosion may occur;

Area No. 2, or area of immunity where metal although remaining bare, does not suffer any corrosion; and

Area No. 3, or area of passivation where the metal is covered with an oxide film.

Besides outlining these areas by experimental means, he also plotted two straight lines on the potential-pH graph defining the area of thermodynamic stability of water under one atmosphere of pressure. These lines are also shown on the potential-pH graph.

The area below Line A is that area in which hydrogen will evolve according to the reaction $2H^+ + 2e^- \rightarrow H_2$ and the area above Line B, in which evolution of oxygen is

possible according to the formula: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

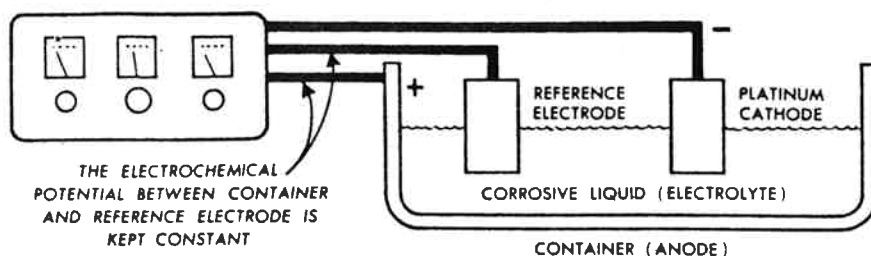
From this diagram, it is possible to predict behavior of iron in solutions of varying pH and also the potentials at which iron will corrode, be under cathodic protection, or possibly be passivated.

How to stop corrosion

You will note, to quote from Pourbaix's work, that the well-known corrosion of iron in ordinary waters, results from the fact that there exists in the centre of the diagram, a great dangerous triangle within which the potential of iron is usually located". He goes on to say that: "we may thus avoid corrosion by three groups of methods: by driving the representative point, respectively, down, up, or to the right that is—

(1) we may lower the potential, and this happens in the case of cathodic protection;

(2) we may make the potential higher, and this occurs when the passivity is due to an oxidizing action;

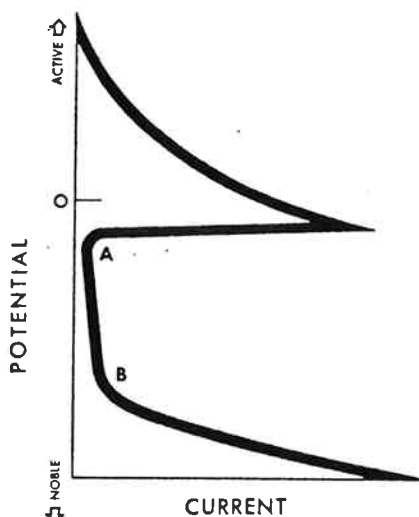


How controller operates

Immersion of the reference electrode in the corrosive fluid (as shown above) establishes an electrochemical cell with the vessel, which forms the other half cell. The meter measures the total voltage developed by this cell and indicates any change in potential of the vessel.

To obtain anodic passivity, a DC current source is connected with its positive terminal to the vessel and its negative terminal to an inert electrode, a platinum-clad electrode unaffected by the liquid.

By shifting the applied potential and recording the values of the current, the "anodic polarization curve" (as shown right) is obtained. In the applied potential



range between points A and B, corrosion is minimized or ceases, and the surface is said to be passive.

(3) we may also render the solution alkaline, but we must then keep the solution sufficiently oxidizing to avoid the small corrosion triangle which exists at the bottom and right-hand of the triangle. It is this triangle, more important at high temperatures, that is responsible for the type of boiler failure known as *caustic cracking*.

Concerning protection by passivation, it must be remembered that the formation of an oxide layer does not necessarily prevent corrosion, for oxide films are not always protective. Often they do afford protection, for instance, in many cases, for iron, aluminum or chromium; sometimes, they do not, as in the case of many metals in chloride solutions.

These Pourbaix diagrams can be made up experimentally for different metals in different aqueous environments, and the areas of immunity, corrosion and passivation can be delineated and, when used in conjunction with polarization curves, much

useful information can be gained concerning corrosion processes. Rather than pursue the theoretical aspects of anodic passivation, we will outline the results of some modern work, using this useful concept.

Dr. Mueller of the Pulp & Paper Research Institute of Canada, initiated experiments in anodic passivation, as early as 1954, concentrating on the corrosion behavior of steel in sulfate pulping digesters. He found that passive films can be produced on mild steel in alkaline pulping solutions by the passage of suitably controlled electric currents from the steel surfaces to the solution. Practical application of this experimental work has been made in full-scale tests which have been fully reported† to the Technical Association of the Pulp & Paper Industry.

Conoco develops controller

More recently, a research team at the Continental Oil Company's Research Department in Ponca City, Oklahoma, undertook extensive anodic

passivation studies on a variety of materials and environments, and developed a high current potential controller to aid them in their investigations.

The phenomenon of anodic protection had been regarded, until this time, as little more than an interesting laboratory curiosity. Its lack of ready acceptance in the industry, stemmed from the special conditions necessary for its application and the dangers inherent in its misuse.

Re-examination of Pourbaix's diagram, would suggest that the maintenance of a vessel in the passive range may be difficult indeed, especially if contamination of the environment occurs, causing shifts between passive and active areas. Also, changes in pH, immediately adjacent to the passive electrodes, would also shift the specimen under protection from a passive to an active condition.

Polarization curves

The behavior of corroding systems where some of the variables, i.e., temperature and concentration, can be held constant, can be accurately investigated by means of plotting surface potential changes of the metal concerned versus current densities (polarization curves), and weight loss data from coupons in these environments held for periods of time within certain potential ranges.

Figure 2 shows a typical polarization curve for a sample of 316 stainless steel in 67% sulfuric acid. Weight loss data indicated that corrosion occurred when the potentials were in the cathodic range, i.e., more negative than 50 millivolts to a calomel reference electrode, and a coupon showed negligible weight loss when potentials were held in the anodic range between +50 and +650 millivolts to the same reference.

Figure 3 shows relationship between potential and weight loss of stainless steel exposed for one hour in a 67% by weight H_2SO_4 solution at 75F. The results of many experiments indicated, that when a metal electrode is taken through a range of potentials in corroding environments, the current density increases initially almost linearly with the change of electrode potential, reaches a peak called the "Flade Point", and then drops very quickly after this Flade arrest point has been passed. This sudden drop in current density is due to the formation of a highly-resistant passive film on the surface of the previously corroding specimen.

†T. R. B. Watson—"Electrolytic Corrosion Protection of Paper Mill Equipment" TAPPI—Vol. 44, No. 10, October, 1961.

Conoco's experiment

In the case of stainless steels in H_2SO_4 , the resistance of this film is very high indeed, e.g., the film resistance of Type 316 stainless steel passivated by electrical means in 67% H_2SO_4 had a calculated film resistance of 17,400,000 ohms per sq. cm. The high resistance of this passive layer, results in a very useful phenomenon called "throwing power", which can best be described in the following experiment undertaken by the researchers at Continental Oil.*

"A 60-ft. piece of $\frac{3}{4}$ "-304 stainless steel tubing had thirteen 180° bends and two 90° bends. A centrifugal pump and a 20-litre reservoir of sulfuric acid, were used to circulate acid through the piping. Acid was circulated for 17 hours, with no protection.

"Periodic samples were obtained, and analyzed for iron content. The iron content increased to over 1,000 parts per million in 17 hours. The acid was removed, the entire system cleaned by a water rinse, and a fresh batch of H_2SO_4 was then placed in the experimental system.

"In the anodic protection experiments, the platinum and calomel reference electrodes were placed at three different locations designated on a schematic of the experimental set-up shown in Figure 3. In location No. 1, both electrodes were installed in an electrically-isolated area, remote from the circulating system. No measurable iron was found after 24 hours.

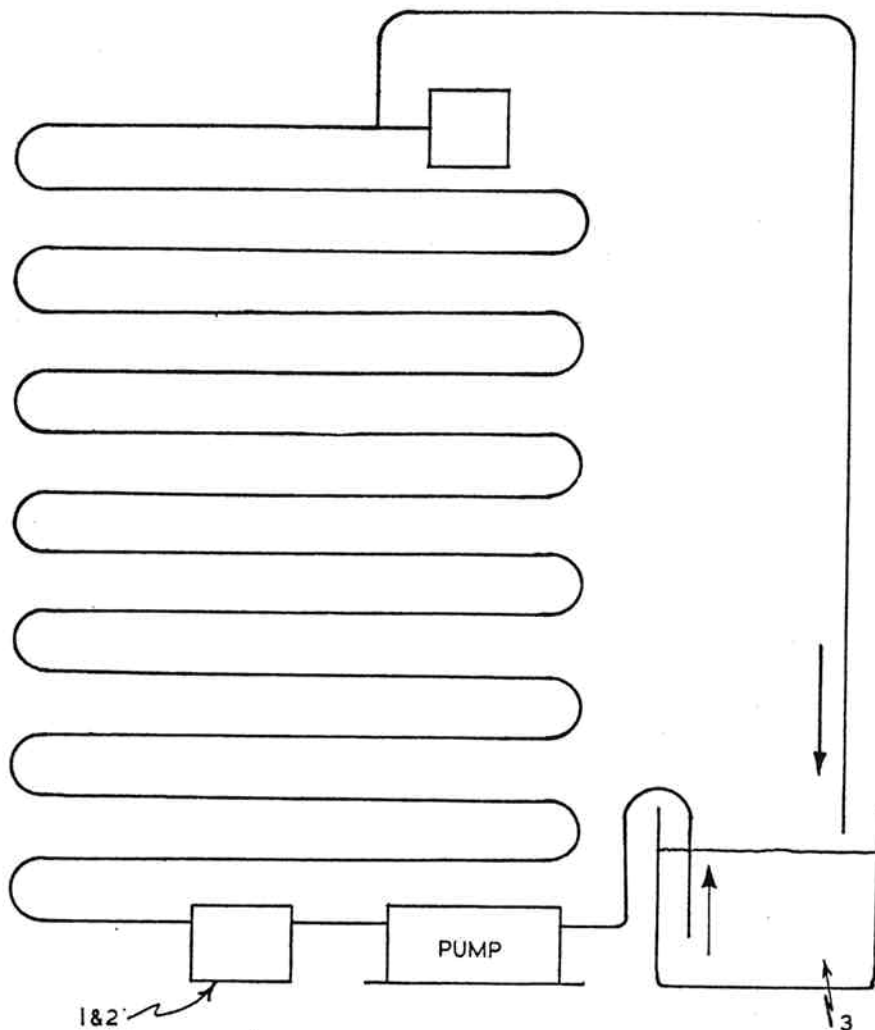
"In the second location, the calomel cell was removed, and the platinum electrode in location No. 1 was used as both cathode and reference electrode. A very slight increase in iron content occurred in 90 hours.

"In the third location, both platinum and calomel cells were installed in the glass reservoir, remote from the circulating system. After 24 hours, some iron was found in solution, but the corrosion rate was still negligible compared to the blank.

"At the conclusion of the experiment, the stainless steel tubing was split and the interior examined for any evidence of corrosion on the base metal or at any of the numerous welds in the system. No evidence of damage was seen."

Current migrates extensively

It is unusual for the applied protective currents used in cathodic protection to penetrate more than a few diameters up a pipe opening, if the anode is exterior to the piping system. Yet, this experiment indicates that the



Conoco's set-up to determine effectiveness of anodic protection. Fig. 4

current migrated easily through the entire piping system, keeping the passive film in repair.

The calculated film resistance for Type 304 stainless steel in 67% acid, is only 224,000 ohms per sq. cm., which is much lower than the calculated film resistance in the same environment of Type 316 stainless steel. Apparently, in the case of stainless steels in sulfuric acid environments, the anodic passive films will permit the use of these electrical protection methods on vessels of the most complex configurations.

Anodic protection can be applied to a wide variety of metals in an equally wide variety of chemical services, if the anodic passive ranges are defined, and if suitable potential control equipment is used to ensure that the potential of the metal surface stays within the required potential ranges. Some of the passive films produced have a relatively long life, and on-off type controllers are suitable for maintaining this film in repair.

This is true in the case of mild steels in concentrated acid service at

ambient temperature, but more sophisticated potential control equipment is required when the acid becomes more dilute or the temperature is raised. The Anotrol potential control equipment is offered to industry by the Anotrol division of Continental Oil Company, who undertake the engineering assessment required for the adaptation of their equipment to specific environmental problems.

This technique seems to be of immediate practical value in stainless steel and mild steel equipment used to store, process and transport such corrosive chemicals as H_2SO_4 , H_3PO_4 , $NaOH$, $LiOH$, $Al_2(SO_4)_3$ and NH_4NO_3 , and experience has shown that lab evaluations of any particular system can be extrapolated with reasonable confidence to field performance.

Items of equipment made passive by anodic protection techniques include: tank cars handling ammonium nitrate () and storage tanks handling sulfuric acid ().

*Anodic Passivation Studies—J. D. Sudbury, O. L. Riggs and D. A. Shock. CORROSION—Vol. 16, No. 2, February (1960).