

Corrosion Control by Anodic Protection

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It is well known that corrosion can sometimes be controlled by cathodic currents and, even with an elementary knowledge of electrochemistry, it is easy to appreciate why this should be so. Corrosion involves the oxidation of the metal and it is reasonable to expect that cathodic polarisation, which discourages oxidation and favours reductions at the metal surface, should tend to cause protection. In fact, the position is somewhat more complicated and, in many cases, other factors override this apparently simple one.

It is not so well known that corrosion can also be prevented in suitable cases by anodic polarisation, and it is certainly very much more difficult to understand why this should be so from the somewhat oversimplified theory of corrosion which the non-specialist is bound to have. It is probably because of this that this method, which is extremely powerful and is often applicable just when cathodic protection is not possible, has not been easily accepted as a practical proposition and is still regarded as only a laboratory curiosity. There is, it seems, a feeling, perhaps unconscious, that the method is basically unsound, and the purpose of the present paper is to explain, in as simple a way as possible, why anodic protection is possible, and when it may be expected to be useful.

General Principles in Corrosion Control

If the "brute force" methods of corrosion control such as plastic, glass or other coatings are neglected, there are two basic methods of corrosion control available. One is to reduce

The technique of cathodic protection is well known and has been widely applied to a number of corrosion problems. It is not so well known that corrosion can also be prevented in suitable cases by anodic protection, using a platinum electrode system. The author shows that, with adequate laboratory work beforehand and proper instrumentation, the use of anodic protection can make an effective contribution to the life of a chemical plant.

the driving force available for corrosion to a minimum, and the other is to ensure that the corrosion product itself stifles the reaction by forming a suitably protective film.

Using the terminology devised by Pourbaix (1), we say that we make use of immunity in the first case while in the second we depend on passivity.

In practice we can achieve immunity by doing one or more of the following:

- (1) Using a suitably noble metal
- (2) Removing unnecessary oxidising agents (e.g. air)
- (3) Adding a cathodic inhibitor (lessening the effectiveness of the oxidising agents)
- (4) Applying cathodic protection

In chemical plant it is often not economic to use noble metals, and if the solutions are highly oxidising the other methods are inapplicable.

Passivity is achieved by:

- (1) Using a metal having an oxide (or other similar corrosion product) which is virtually insoluble in the medium
- (2) Ensuring that sufficient oxidising agent is always present for the oxide to be formed
- (3) Applying anodic polarisation to maintain the oxide in constant repair

In principle therefore anodic protection has much in common with the practice of adding oxidising substances such as chromates or nitrites as inhibitors. Cathodic protection on the other hand is, in some ways, related to practices such as de-aeration.

The similarity can be taken further. In a metal/solution system in which corrosion is low because of immunity, corrosion is generally enhanced by either the addition of oxidising agents or by anodic polarisation, while in a case depending on passivity it is dangerous either to de-aerate or to apply cathodic currents.

Protection of Ferrous Materials in Acid Solutions

Anodic protection will probably prove most useful with iron-based alloys in acid solutions and for this reason this case has been selected as an example. Fig. 1 shows the Pourbaix diagram (1) for iron; the conditions for passivity and immunity are indicated. From this it will be seen that, in acid solutions, there is a considerable gap of potentials over which neither of these conditions is established and which should lead to heavy corrosion.

Lines A and B in this diagram refer to the lower and upper limits of stability of water. Above A water is oxidised to oxygen and below A it is reduced to hydrogen.

If we place iron in a strong acid solution we can in theory protect it cathodically by lowering its potential to the region of immunity. However, since water is not stable at such low potentials, continuous and rapid hydrogen evolution will occur. This is not a

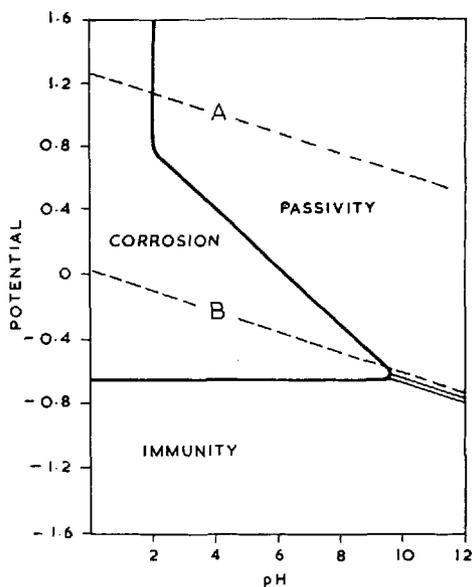


Fig. 1 Pourbaix diagram for iron in aqueous solutions

practical way of avoiding corrosion both because of the very heavy current requirement and because there is little point in preventing corrosion if to do so we have to decompose the solution.

Raising the potential of iron by anodic polarisation or by the addition of a suitable oxidising agent to sufficiently high values for passivity does, on the other hand, seem to be a more promising way of avoiding corrosion. This is particularly so since the area of passivity for iron, and especially for some of the iron-chromium alloys, is considerably larger than indicated by Fig. 1 which was obtained by calculation after making certain assumptions.

The actual relation between potential and corrosion rate at a given pH is shown diagrammatically in a somewhat simplified manner in Fig. 2. This is an experimentally determinable curve for any given solution and alloy by using the potentiostatic techniques which are becoming widely used in corrosion studies (2). From Fig. 2, which is typical of many cases, it can be seen that once the potential is raised sufficiently to establish

passivity the corrosion rate falls to really negligible values. For example with iron in normal sulphuric acid the rate falls to approximately $0.1 \text{ mg/cm}^2/\text{day}$ and the current density necessary to maintain passivity is $5 \mu\text{A/cm}^2$. The rate of corrosion of passive iron in this acid is therefore negligible and iron could be a very satisfactory container material.

It is important to appreciate at this stage that the rate of corrosion of a metal in a given acid solution is an accurately determinable property *provided* the potential is specified. The highly scattered and apparently meaningless results often obtainable on conventional corrosion "test specimens" are entirely due to the potential wandering in an uncontrolled manner, but once results such as those in Fig. 2 have been obtained for a given metal/solution system we can fully depend on them in practice, again *provided* we also ensure that the potential of the plant relative to the solution is kept at the correct value. Alternatively we can monitor accurately the rate of corrosion by measuring the potential and referring to Fig. 2.

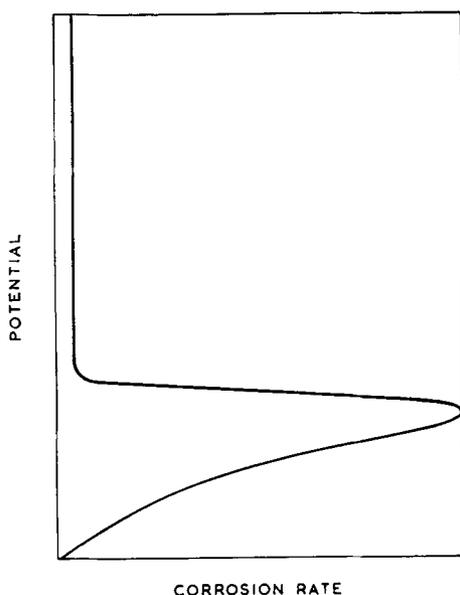


Fig. 2 Relation between potential and corrosion rate for iron in sulphuric acid

From the above it must have become obvious that anodic protection is simply a way of ensuring that the potential of the metal is kept sufficiently high for passivity to be stable.

Instrumentation

If the potential of iron is raised appreciably above line A in Fig. 1, oxygen evolution takes place (i.e. the solution starts being decomposed and current is wasted) so that this imposes an upper limit to the desirable potential. With the stainless steels oxygen is not generally evolved, but the corrosion rate increases above a certain potential so that again there is an upper limit for the potential. With titanium (3), and some other metals which form non-conductive films, there is generally much greater latitude and it is often possible to raise the potential by some tens of volts, but in these cases too the protection can break down if the potential is raised sufficiently.

The important fact is that there is an upper, as well as a lower, limit to the range of potentials which give satisfactory results. This means that the instrument required for anodic protection is a "potentiostat" but the exact nature of the instrument depends greatly on the system.

If the range of satisfactory potentials is large, as with titanium, a very simple constant voltage device such as an accumulator or even a dry cell will meet the requirements. In such a case it can safely be assumed that the potential of the inert cathode will not wander by more than a few hundreds of millivolts no matter what the current may be, and if the potential between the cathode and the plant is kept sufficiently great there will be no danger that the potential of the plant will fall to the breakdown point. Cotton has in point of fact found this system completely satisfactory for titanium in hydrochloric acid.

This simple method should also be applicable in certain cases for ferrous alloys, even though the useful potential range is only a few hundreds of millivolts but, in general, it

would be safer to use a true potentiostat. This instrument measures the potential of the plant against a standard electrode, and maintains it at the desired value by passing a polarising current through an inert auxiliary electrode.

There are numerous potentiostat circuits available and the laboratory types are fully electronic and can control potentials very accurately but have a rather low current output. For industrial use output is the main requirement, and a servo-operated instrument would be more satisfactory.

The cost of equipment for anodic protection should not be high even if a true potentiostatic system is called for but, if the method is to be used to best advantage, it is worth installing, at the same time, a monitoring system to provide a record of the performance of the plant from the corrosion point of view (4). This could also provide a warning should anything unforeseen occur.

The position is exactly analogous to the use of a temperature controller on, for instance, a furnace, which will protect the furnace from overheating, but, without a temperature recorder or at least an indicator, the system is incomplete.

Dangers and Limitations in the Application of Anodic Protection

The method is particularly suitable for application in the heavy chemical field, but the solutions handled in chemical plant differ so greatly that each case has to be studied on a laboratory scale before anodic protection can be safely applied.

This preliminary work must include a metallographic study, since there are various types of corrosion such as intercrystalline corrosion and selective attack that can limit the use of alloys to a smaller range of potential than might be appreciated (5).

The greatest danger comes, however, from the shape of the curve sketched in Fig. 2. In this it can be seen that at potentials just below those at which protection establishes

itself, the rate of corrosion is very high. In some cases this rate can be many orders of magnitude greater than that of the passive metal. If a vessel were to go active, in order to re-establish passivity the protective device would have to be able to supply a current equivalent to the highest possible rate of corrosion. This means that the potentiostat must be able to provide a current many orders of magnitude above that necessary for protection, and if it cannot it may lose control. This is the reason why monitoring is thought to be advisable. This danger may be one reason why the method has not found much support up to now. Serious as it is, it has certainly been overstated possibly because, in an effort to demonstrate the spectacular possibilities of the method, the solution used in the first pilot plant experiments was one of the most difficult to handle (6). In that case the potentiostat available was highly inadequate for the purpose (having been constructed for laboratory studies on small specimens) and could supply a current great enough for protection, but there was little in hand to allow for even small local accidents. Nevertheless the plant ran successfully for many hundreds of hours. More recent American work (7, 8, 9) has shown that the risk is not unduly great, and with suitable instrumentation it should be possible to overcome this difficulty entirely.

It is not possible to enumerate all the limitations of the method but it is just worth pointing out that not all metals show an adequate range of passivity, and that with any given metal passivity will not be stable in all solutions. The method depends on an electrolytic current arriving at the metal so that it is inapplicable above the wash line in a vessel or in similar places.

Applications of Anodic Protection

Although there have been some reports in the technical press (9, 10) of the use of anodic protection, and there have been a few other trials, the method has as yet hardly been tried in practice.

From a corrosion point of view all chemical plant tends to be grossly over-designed, since it is like a furnace without a temperature controller or recorder. The scope for the use of protection and/or monitoring is therefore enormous. With stainless steel plant, for instance, it is usual to maintain acid strength, temperatures, pressures or other such variables below values which give trouble. Since there is generally no means of telling how near the plant is to losing passivity the materials are not used to their limit. Another way of saying the above is that unnecessarily expensive grades of material are usually selected for chemical plant in order to provide some degree of safety.

It seems that it is possible to make a distinction between two uses of anodic protection. In the first instance it should be possible to employ it in order to allow existing plant and materials to be used to their limit, with anodic protection and/or monitoring only as a safety device. With courage however there seems no reason why plant should not be specially designed from inferior materials which would depend for survival entirely on anodic protection. In this case, of course, the anodic protection system may have to be expensive but the economics could turn out to be attractive if there were a substantial saving on construction material, or if the plant could be run under conditions much beyond anything that could be visualised without protection.

Plant and Electrode Design

There seems to be only one plant design feature to take into account. An electrolytic current must flow to the plant for protection. The current necessary is generally lower than $10\mu\text{A}/\text{cm}^2$, and it is relatively easy to calculate how far it will "throw" if the conductivity of the solution is known and if the available voltage range has been established. In practice it is found that the throwing power is enormous, as has been demonstrated by recent American work (9), and reasonably long tubes can be protected easily provided

the solution is a good conductor. Naturally, it is somewhat more difficult to deal with an accidental breakdown at the end of a tube than inside a vessel, but it is relatively easy to assess the risks involved.

It is not possible to protect above the wash line in a vessel where corrosion may be due to spray. Some parts of valves and pumps are also difficult, but there is no reason why materials which are naturally resistant should not be used at the danger points in conjunction with inferior materials elsewhere. Provided the materials are suitably selected there should be no complications with stray currents.

In so far as electrodes are concerned the standard, if used, could be similar to that which would be used for pH measurements in the same medium. Bearing in mind however that the accuracy required of the standard for this application is not great, very simple and robust standards could be used instead. For example, a platinum wire responding to the natural redox potential of the solution would be adequate if this were reasonably stable.

As far as the cathode is concerned there is again considerable latitude, but it is worth remembering one point. If a potentiostatic system is used there may be short periods when the polarity of the current is reversed so that the cathode becomes an anode. For this reason if this electrode is made from, say, copper or nickel, in the hope that it will be protected cathodically, it may well vanish during these reversals of polarity and, for this reason, it is felt that noble metals are more convenient. Platinum is a natural choice because of its good electrical conductivity, low hydrogen overvoltage, good sealing to glass and not least the ease of cleaning were a deposit to be formed as a result of the passage of a current.

Summary and Conclusions

From a corrosion point of view anodic protection is, to a chemical plant, what a temperature controller is to a furnace. With-

out anodic protection chemical plant has to be oversized and best use is not made of materials.

The method has hardly been used in practice although it is simple to apply. This is probably partly due to an inadequate understanding of how the method works and a feeling that it is a laboratory curiosity. In

point of fact there is nothing more strange in protection by an anodic current than there is in protection by oxidising agents such as chromates, which are universally accepted.

There are of course dangers and limitations but, with adequate laboratory work and suitable instrumentations these do not amount to a serious objection to the technique.

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Properties of Platinum Metals and Alloys

AN ANNOTATED BIBLIOGRAPHY

The literature dealing with the properties of platinum and the platinum group metals is, on the whole, sparse and widely scattered. On this account a recent publication, called a "technical phase report", prepared by R. W. Douglass, F. C. Holden and R. I. Jaffee, of Battelle Memorial Institute for the U.S. Office of Naval Research, is particularly welcome. This was written with the special intention that it should serve as a guide to planning experimental work on the platinum group metals, "revealing", as the authors put it, "areas where concentrated study is needed and preventing duplication of previous work" and was produced as the first part of a study at Battelle of the metallurgical properties of the refractory platinum group metals.

As it is presented, this report provides a very careful survey of the literature of the past fifty years on the properties of the metals and on the constitution of their binary alloys, listing 281 references.

The review of this mass of literature extends to 105 pages and is reasonably comprehensive. The publication as a whole is likely to prove an invaluable source book to anyone interested in the literature of the platinum metals, but it is rather less valuable as a critical survey. The brief introductory notes on extraction and beneficiation are, for instance, misleading as far as modern conditions are concerned, for today South Africa is undoubtedly the most significant world source of the platinum metals. A few of the figures quoted for the physical and mechanical properties are certainly in error—at least as far as the pure metals are concerned—and need to be treated with much more reserve than is accorded them by the authors. However, if this is treated as a first-class annotated bibliography—which it primarily is—the report will be found a most useful work of reference by all interested in the platinum metals.

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