

ANODIC PROTECTION OF CONTINUOUS DIGESTERS TO PREVENT CORROSION AND CRACKING

J. Ian Munro, P. Eng.,
Manager of Technical Services,
Corrosion Service Company Limited,
369 Rimrock Road,
Downsview, Ontario, Canada.
M3J 3G2

ABSTRACT

Anodic protection has been shown to prevent corrosion of continuous digesters. Research indicates that this type of protection will also prevent caustic cracking in both soda and kraft vessels. The purpose of this paper is to familiarize pulp mill personnel with the basic mechanisms of corrosion and caustic cracking in digesters and how anodic protection can be utilized to prevent these serious problems.

INTRODUCTION

Recently, caustic cracking of continuous pulp digesters has become a serious concern to many mills. Inspection and repair costs including loss of production due to outages have become significant. Anodic protection is one of several possible solutions being investigated by a T.A.P.P.I. committee. Anodic protection of a pulp mill digester was first installed by Mueller and Watson in 1956 on an indirectly steamed batch vessel. Data from this and other installations indicated reduction in general corrosion rates from approximately 73 to 4 mils per year(1). In 1978 Hammermill Paper installed the first anodic protection system in a continuous digester(2). The system was used to prevent general corrosion of the upper sections of the soda vessel.

Singbeil and Tromans published work (3) indicating that digester steel can caustic crack in both soda and kraft liquors under certain electrochemical and stress conditions. Their work provides the theoretical background for the use of anodic protection to prevent caustic cracking in pulp mill digesters. Recently several continuous kraft digesters have been anodically protected in an effort to prevent caustic cracking.

Corrosion and Cracking in Caustic Environments

When a metal is placed in a solution, a reference electrode and voltmeter can be used to measure the electrochemical potential of that metal as shown in Figure #1. Changes in the solution chemistry and/or application of an electric current.

For the majority of metal-electrolyte combinations, addition of an oxidizing species such as nitric acid or oxygen results in a more positive metal-to-electrolyte potential with a corresponding increase in corrosion rate. A relationship between corrosion rate and oxidizing power, as illustrated in Figure #2 exists for several metal-electrolyte combinations. For instance, mild steel in caustic concentrations greater than 0.5% by weight exhibit this behaviour.

At the intermediate values of oxidizing power the corrosion rate increases, however, at a critical oxidant level the corrosion rate decreases significantly, due to the formation of a passive film. If the chemical conditions are favourable, the metal (steel in this case) will corrode at a very low rate. Unfortunately, due to process upsets, changes in chemistry or temperature variations, the metal can enter the active region resulting in increased corrosion. The corrosion rate versus oxidizing power graph can be determined experimentally utilizing a potentiostat (Fig. #3). The potentiostat can simulate changes in oxidizing power without the need for chemical additions. The current density is proportional to the corrosion rate while the potential of the metal is analogous to the oxidizing power in Fig. #2.

Caustic Cracking

To this point the only possible states of the metal discussed have been active or passive, corresponding to high or low corrosion rates respectively. Unfortunately, both of these states can co-exist on a single metal sample.

As the average potential of the specimen moves from the passive region to the active passive transition, the protective film becomes unstable at discrete locations. Singbeil and Tromans (3) have shown that if the tensile stress in the metal is large, caustic cracking can occur at locations of film breakdown. The important conclusion from this research is that caustic cracking will only occur if the steel-to-liquor potential is confined to a narrow band near the active-passive transition. Movement of the steel potential in an anodic or cathodic direction away from this cracking zone should therefore prevent the possibility of caustic cracking.

Electrochemical Protection

As previously implied, the operating potential of a vessel can be changed by chemical additions or by the application of an electrical current to the metal. Chemical additions are costly, usually result in process contamination and cannot be injected at a high enough rate to overcome process upsets.

Electrochemical protection systems can overcome all of the problems associated with chemical additions. Figure #4 outlines the three most common types of electrochemical protection systems.

Although caustic cracking should be mitigated by either anodic or cathodic protection, the type of protection utilized has a far reaching effect on the resulting corrosion rate of the vessel.

When a structure caustic cracks, the majority of the metal is spontaneously passive. Only the small inadequately filmed locations must be forced passive. Usually this does not require a large amount of current. Once passive, the amount of protection current decreases with time. Forced passivation is accomplished by moving the vessel potential slightly positive until the film is completely stable. In this case the vessel is made more anodic and hence is anodically protected. The anodic protection simply creates the conditions necessary to allow the steel to form a passive film.

The cathodic protection technique has inherent limitations in caustic environments. The amount of current required is enormous, resulting in installation of very expensive impressed current anodes which possess a finite lifetime. Assuming a vessel is on the verge of complete passivity, the current density required for protection is at least as great in magnitude as the difference between the passive and active-passive current densities shown on the potentiodynamic curve in Figure #3. This cathodic current must be maintained as the current will not decay with time. The major shortcoming with cathodic protection is the possibility of some part of the vessel stabilizing at a potential E_{pp} resulting in cracking and/or high corrosion rate. It is also impossible to protect air electrolyte interfaces with cathodic protection. Anodic protection therefore is the only practical electrochemical method to prevent digester corrosion and caustic cracking.

Anodic Protection Design

Figure #5 indicates the basic electrical layout of an anodic protection system. The protection scheme is composed of an auxiliary cathode, a reference electrode and a potential controlled rectifier. Although the basic concept of anodic protection is relatively simple, the engineering of a durable low maintenance system to be installed in a high temperature and pressure continuous digester is complex. The protection hardware must be durable since failure of internal equipment not only results in lack of protection but can interfere with operation of the outlet device resulting in digester downtime.

Cathode

The cathode is an isolated metal electrode installed to allow current flow from the digester wall to the liquor. There are many design considerations necessary to fabricate a long life cathode. Firstly, the electrode must not interfere with the digester operation. Interference with the chip/liquor plug flow is not acceptable. The cathode must be structurally sound to withstand normal flow conditions as well as the possibility of back flow. In order to serve as a rectifier powered cathode, the metal must be electrically isolated from all digester components. Leads through the digester wall must also be isolated and sealed against the digester operating pressure. Surface area of the cathode is critical to ensure that the metal is cathodically protected and therefore does not corrode. All isolation materials must be fluorocarbon to withstand operating temperatures.

There are several electrical design considerations important to the correct operation of the cathode. Due to the high current density on the cathode electrical attenuation can occur. The manifestation of this effect is that significantly larger current densities will arrive on the cathode near the electrical connections. Electrical attenuation must be minimized to ensure uniform current density and hence adequate protection over the entire digester shell.

Figure #6 depicts the conceptual cathode design. All of the aforementioned design considerations have been addressed. An early version of the cathode has been operating in a soda digester for over five years with no reported problems. Many small modifications have been utilized to minimize installation time. It is sometimes necessary to reroute the 4" O.D. liquor line on Kraft digesters if the line is in use. If not, the liquor line is removed.

Reference Probe

Anodic protection systems control the digester to liquor interfacial potential to a predetermined value. This potential must be measured between the digester and a reference electrode which is a critical part of the total system. The more common references such as calomel and silver-silver chloride will not operate in the digester environment owing to the operating temperature, pressure and/or contamination.

Several types of references have been used in conjunction with anodic protection of continuous digesters. A modified calomel reference used by Watson and Mueller in batch digesters has proved

successful, although when the junction becomes liquor saturated, stability is lost. Autoclave research (4) indicated that a molybdenum-molybdenum oxide reference was extremely stable in both soda and kraft liquors at temperatures between ambient and 400°C. Data suggested that the molybdenum reference was not sensitive to variations in liquor sulphidity. Operation in actual digesters confirms the research work on the stability of this metal-metal oxide reference. Further, it has been verified that acid cleaning of a digester does not harm the reference.

Silver-Silver white liquor references have been used in other pulp mill liquor handling systems (5, 6) successfully. Further research is required to confirm the same degree of stability in an operating digester. The major question is whether this reference will return to equilibrium after a digester acid clean. It was determined (2) that this type of reference was not stable in a soda liquor due to the low sulphur concentration. Interestingly, the reference with the largest history of stability in both kraft and soda continuous digesters is 316 stainless steel. Due to electrode kinetics, stainless steel produces an equilibrium potential in the passive potential zone of digester steel.

Conceptually the reference electrodes can be the most troublesome part of the anodic protection system. To date the references have required very little maintenance but the reference probe can be retracted from the digester under operating pressure and temperature. Figure #7 shows the basic monitoring probe.

EXPERIENCE WITH DIGESTER PROTECTION

Corrosion

All of the protection systems undertaken to date have been on single vessel hydraulic continuous digesters. Coupon and inspections have indicated that if the potential is controlled in the passive zone corrosion rates are reduced significantly. In both soda and kraft liquors protected coupon weight loss has been negligible. No areas of the digesters have been found to have accelerated corrosion rates. General corrosion in protected digesters has been virtually eliminated.

Caustic Cracking

The use of anodic protection to prevent caustic cracking is more difficult to verify. Standard cracking coupon tests have not been reproducible in digesters that are not protected (7). Therefore digesters must be inspected to confirm the benefit of anodic protection to prevent cracking. This

results in long delays in receipt of data. Even when data is available showing after a year that cracking is halted, does not necessarily prove the anodic protection was the solution. Perhaps the cracks have not formed as the initiation time has not been exceeded. Several yearly inspections will be required to ensure anodic protection is the ultimate answer.

During the summer of 1981 a protected soda digester was inspected for cracks. It is important to note that a similar inspection had not been carried out in the past. Shallow cracks were found in the transition welds, presumably prior to protection. As a controlled test some of the cracks were removed by grinding. Inspection in 1982 indicated that new cracks had not initiated and that the existing cracks did not propagate.

Inspection of all protected digesters will eventually confirm the effectiveness of anodic protection in preventing caustic cracking.

FACTORS AFFECTING THE STABILITY OF THE PASSIVE FILM

The output of the anodic protection system should be a function of the tendency for the digester to activate. If the cracking and corrosion is caused by a liquor chemistry or temperature changes then protection current should indicate these process upsets.

All system parameters of the anodic protection system are monitored on a continuous strip chart recording in the digester control room. Although current output varies significantly correlation has not yet been found between operating temperature, sulphidity, causticity or type of wood been pulped. Minor liquor constituents such as polysulphides and thiosulphates have not been monitored. One possibility for the lack of correlation is that destruction of the passive film may require a great deal of time. Comparison of process variables with output current would then have to be averaged over long time periods. This averaging is currently being investigated.

One fact that has emerged is that after a digester shutdown the current required to establish the passive current increases ten-fold from the steady state value. As discussed previously, the only digesters protected are single vessel units. As such they are all acid cleaned to ensure proper extraction screen operation.

An indirect conclusion could be that acid cleaning destroys the passive film. However, referring to prior batch digester protection the same increase in current requirements was shown to be a result of fresh liquor impingement on the steel.

Until an impregnation vessel is protected, the ramifications of acid cleaning can not be determined from the anodic protection current output.

References

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The work by Singbeil and Tromans was instrumental in establishing the theory necessary to prevent caustic cracking by anodic protection.

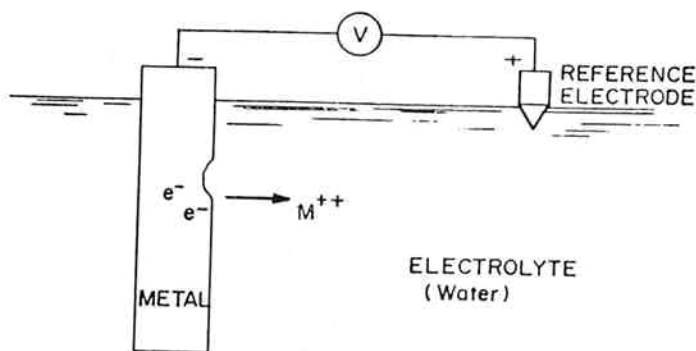


FIGURE #1

MEASUREMENT OF THE SOLUTION POTENTIAL OF METAL
IN AN ELECTROLYTE

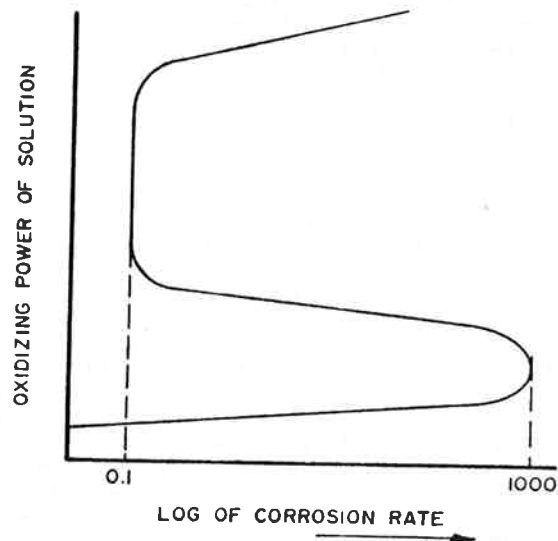


FIGURE #2

CORROSION RATE OF ACTIVE-PASSIVE METAL

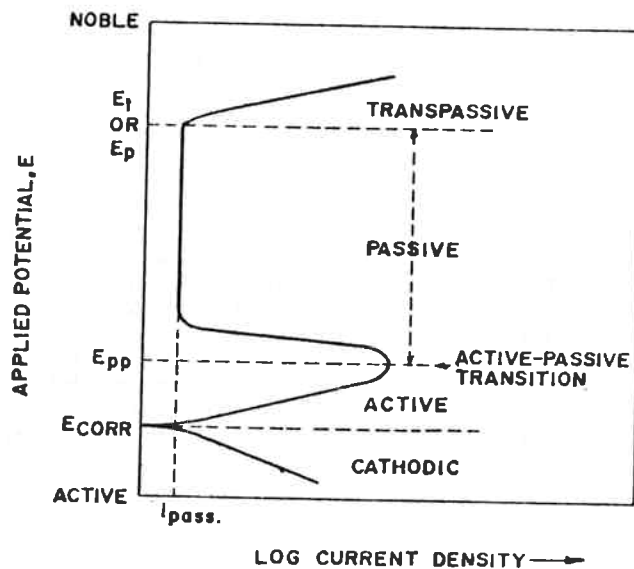


FIGURE #3

POTENTIODYNAMIC CURVE OF AN ACTIVE-PASSIVE METAL

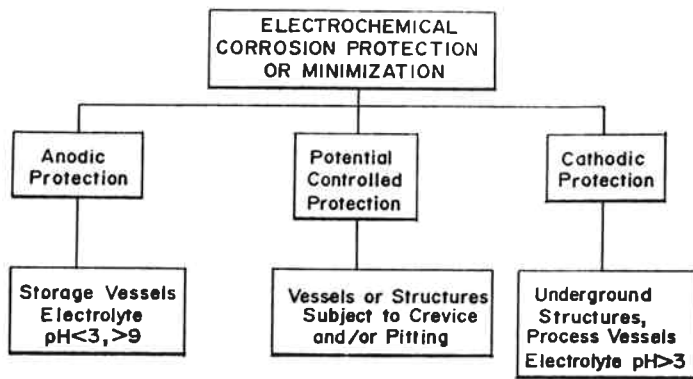
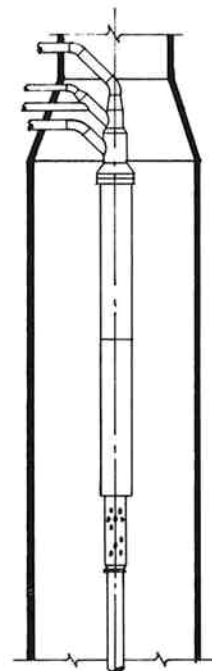


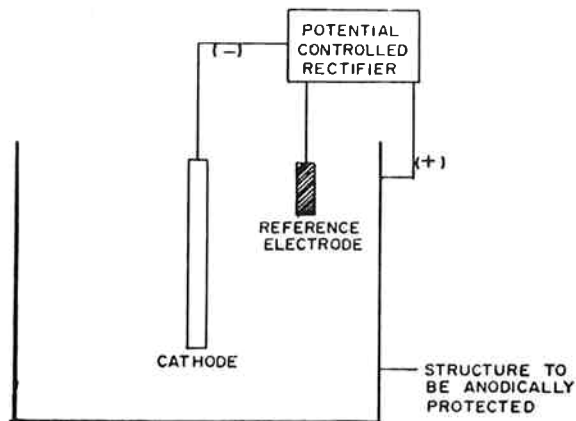
FIGURE #4

CLASSIFICATIONS OF ELECTROCHEMICAL PROTECTION



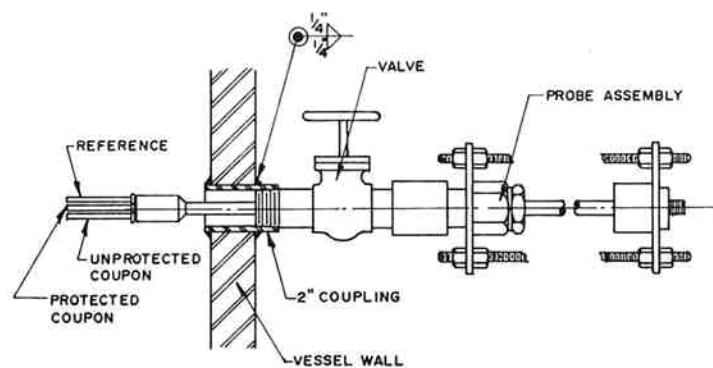
CATHODE ARRANGEMENT

FIGURE #6



SCHEMATIC OF ANODIC PROTECTION SYSTEM

FIGURE #5



REFERENCE PROBE ASSEMBLY

FIGURE #7