

# **CATHODIC AND ANODIC PROTECTION IN THE PAPER INDUSTRY**

by

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**CORROSION  
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## **Cathodic and Anodic Protection in the Paper Industry**

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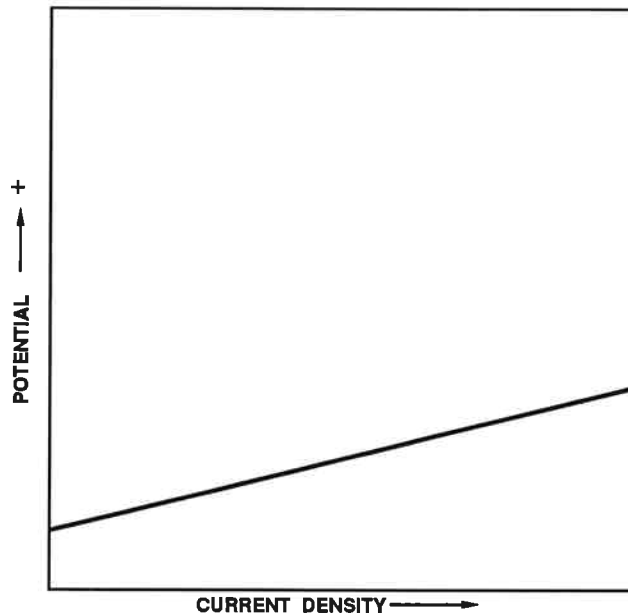
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It is best to review the differences between these two protection techniques before discussing their application in the Paper Industry.

Corrosionists have been aware of the electrochemical nature of aqueous corrosion since the studies of Davy & Faraday. Apart from some early experiments using zinc and iron anodes to protect copper sheathing on ship's bottoms the deliberate application of comprehensive systems to protect steel from corrosion by the technique known as cathodic protection was in hiatus from the time of Davy's experiment in the 1820's to the 1930's. Cathodic protection has been in extensive use only since 1945. In fact, the National Association of Corrosion Engineers was organized by proponents of this technology in the petroleum industry.

Modern electrochemistry for the North Americans commenced in the 1950's where the study of energy transfer in ionic conductors was de-emphasized and the electron transfer at the electrode surfaces was and is being closely studied. Improvements in instrumentation and measurement techniques and, from the viewpoint of the practical corrosionist, the development of dependable, versatile potentiostats permitted a leap forward in the study of surface phenomena on corroding surfaces and as a corollary some hitherto undiscovered techniques for corrosion control.

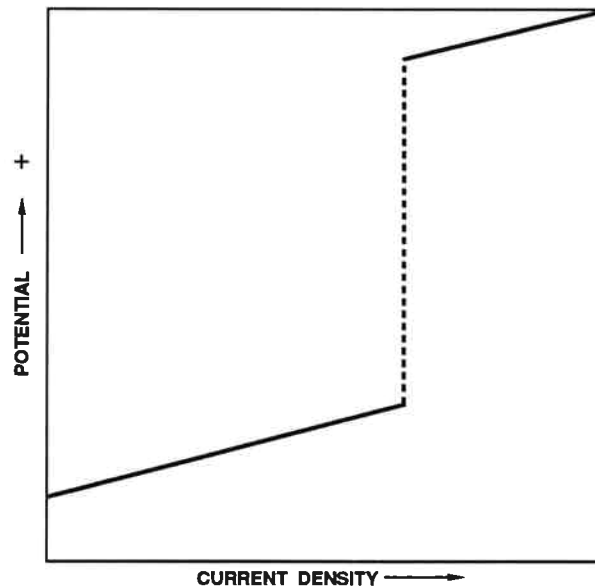
The study of electrode behaviour under dynamic conditions resulted in the plotting of electrode behaviour on graphs in which electrode potential was plotted against current flow to or from the electrode. These graphs were called polarization curves, the earlier ones being called galvanostatic polarization curves since the current flowing to (or from) the electrode was the independent variable and the electrode potential was the dependent variable. Such a curve is shown in Figure 1.



GALVANOSTATIC ANODIC POLARIZATION CURVE

FIGURE 1

This curve was produced by immersing the electrode under examination in a suitable electrolyte and with the use of a counter electrode in the same electrolyte, a DC power source connected between the electrodes and a means of controlling the current in increments points, along the curve could be determined. It was found that with some metals and electrolytes, an area of instability occurred where a very small increase of current would cause a large instantaneous change of potential. This phenomenon is shown in Figure 2.



GALVANOSTATIC ANODIC POLARIZATION CURVE  
SHOWING INSTABILITY

FIGURE 2

This unstable electrode potential range could be studied only by using a potentiostat. This instrument incorporated a DC power supply and a feedback control system that could hold an electrode at a preset potential by automatically adjusting the magnitude of the current being discharged or collected by the electrode under examination. Using this system of control the electrode potential becomes the independent variable and the current the dependent variable. Electronic plotters permitted the recording of rapid current changes and curves such as those shown in Figure 3 were produced. It should be noted that the convention adopted in North America is contrary to mathematical convention that suggests the independent variable be plotted on the abscissa. The North American method of plotting makes it easier to overlay potentiostatic and galvanostatic plots or to compare them to potential-pH diagram where potentials are plotted on the ordinate.

This particular curve was always obtained for a metal electrolyte system that showed instability under galvanostatic analysis. In Figure 3, this curve can be broken up into areas that are descriptive of the condition of the electrode metal when held in those potential regions and examined after a period of time.

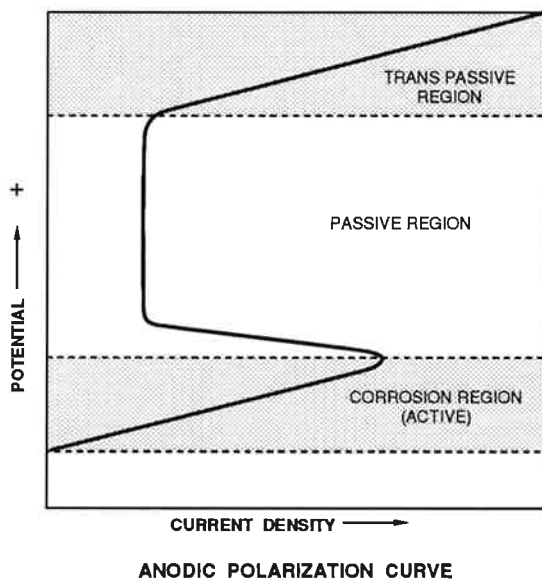


FIGURE 3

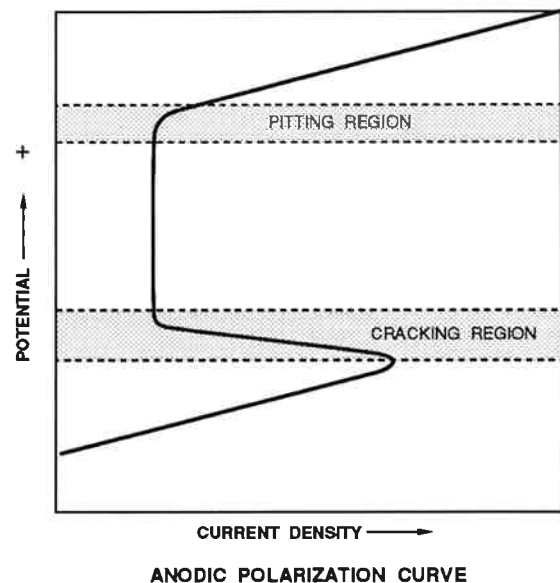
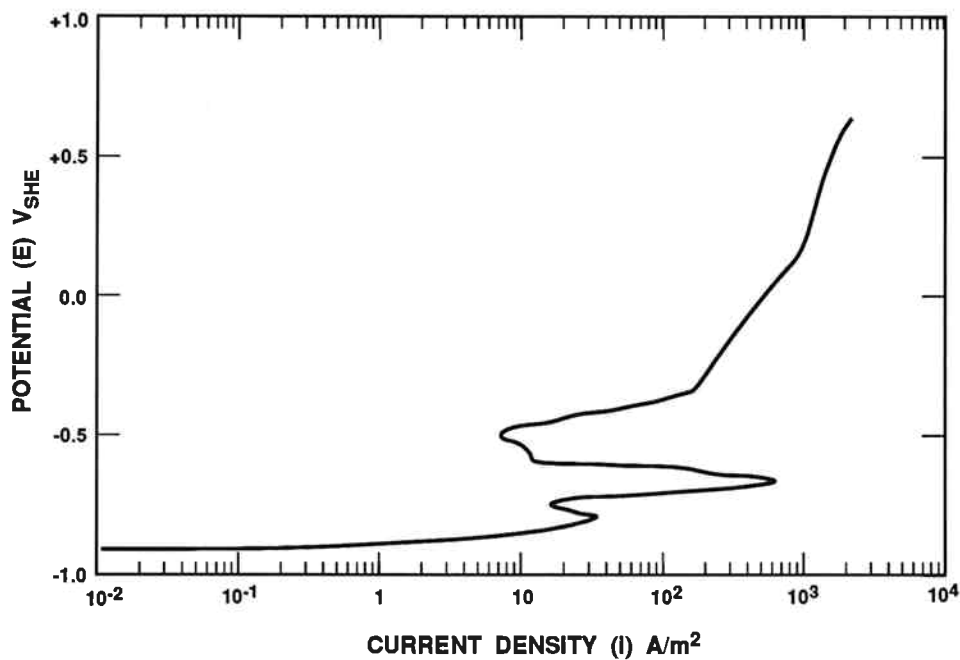


FIGURE 4

The main regions shown in Figure 3 can be further divided into sub-regions identified as pitting and cracking regions as shown in Figure 4. The cathodic region would be shown to the left of the ordinate on Figure 4 at potentials more electronegative than that shown at the intercept with the ordinate.

Metals that show anodic polarization behaviour as shown in Figures 3 and 4 are said to be capable of active-passive transition. Some metals show this behaviour only in specific electrolytes. In general metals that are normally passive such as stainless steels would have polarization curves of this general shape if activated or moved into trans-passive regions. Mild steel in high pH solution or in concentrated sulphuric acid will also show this behaviour.

Actual polarization curves are usually plotted with the current on a logarithmic scale expressed as current density. Figure 5 shows an actual polarization curve taken in a pulping liquor using a mild steel electrode.



**ANODIC POLARIZATION BEHAVIOR OF  
MILD STEEL IN NaOH+Na<sub>2</sub>S SOLUTION**

**FIGURE 5**

Since corrosion rate is directly related by Faraday's equivalent to the current discharged from the electrode, examination of Figure 5 suggests that mild steel in the passive range would exhibit a corrosion rate of more than one order of magnitude less than that anticipated if potentials were in the corrosion or active region.

Pourbaix has displayed the relationship between electrode potentials and pH on his now famous diagrams [1]. On these diagrams he had calculated boundaries that separate regions of immunity, corrosion and passivity. A Pourbaix Potential pH diagram is produced in Figure 6 showing the relationship between this diagram and an anodic polarization curve showing an active-passive transition. Note that the region of immunity stretches across the bottom of the diagram and indicates the potential range in which an electrode will not corrode ie. it is thermodynamically stable.

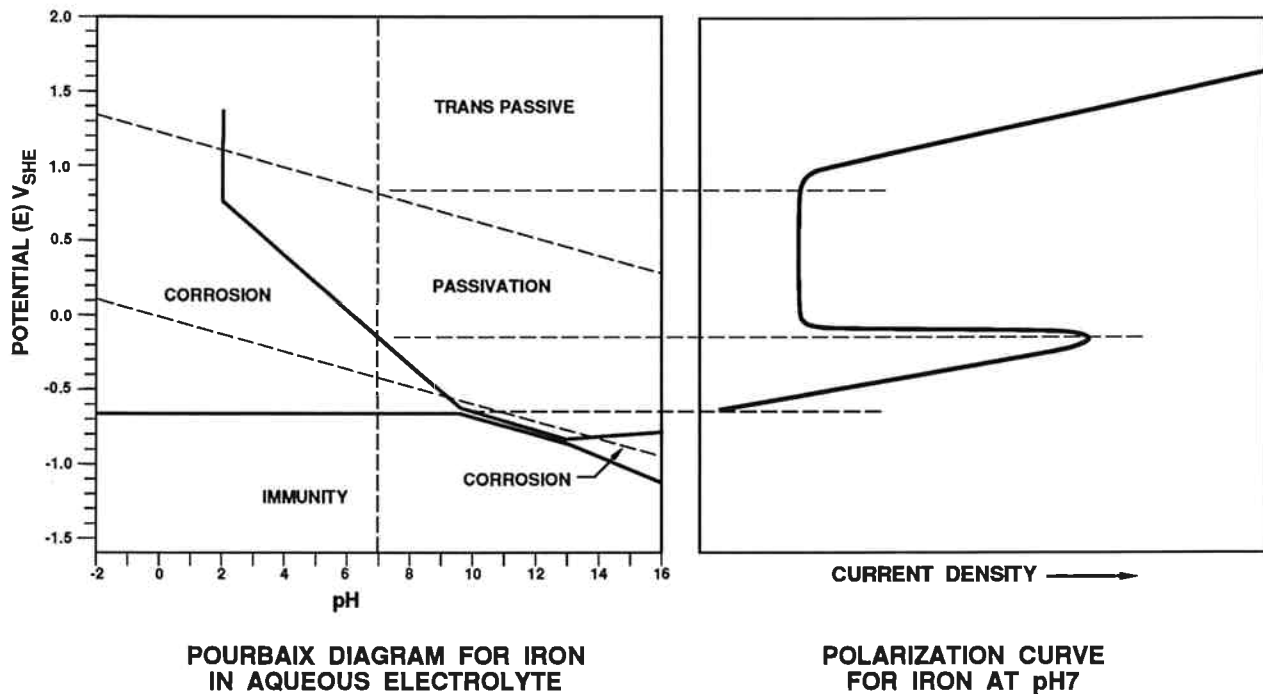


FIGURE 6

Thermodynamics treat only the possibilities of immunity or passivity. Although it is thermodynamically possible to render iron immune from corrosion at pH1, it is practically impossible. Enormous current densities are required to shift potentials in the negative direction since an electrode reaction takes place before the immunity boundary, is reached in which large volumes of hydrogen are released at the electrode surface.

IS-1010

The broad term Electrochemical Protection encompasses three techniques that are applicable in the paper industry. Cathodic protection, anodic protection, and protection by potential adjustment.

Cathodic Protection can be applied to:

- Effluent Treatment Clarifier
- Process and Fire Water Storage Tanks
- Underground Piping Systems (Natural Gas Water)
- Buried Fuel Storage Tanks
- Foundation and Dock Piling
- Deaeration Tanks
- Reinforced Concrete Structures

Anodic Protection can be applied to:

- Continuous and Batch Digesters
- White and Green Liquor Tanks and Clarifiers
- Heavy Black Liquor Storage Tanks
- Caustic and Sulphuric Acid Storage Tanks

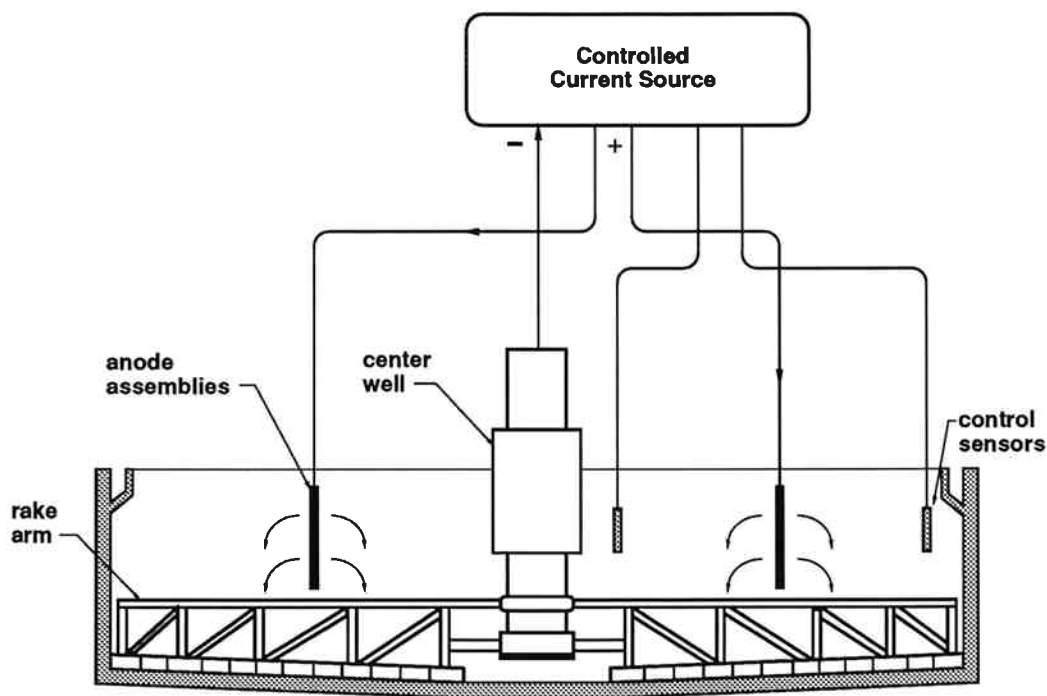
Protection by Potential Adjustment:

- Bleached Pulp Washer Drums (C, CD and D stages)
- Seal Tanks
- Chlorine Mixing Tanks
- Linerboard Brightener Equipment (Zinc Hydrosulphite)
- Sulphur Dioxide Flue Gas Scrubbers
- Continuous Digester to Eliminate Cracking Problems

## **Cathodic Protection**

Apart from underground piping systems and buried fuel storage facilities the paper industry has a large investment in effluent clarifiers. The corrosion on these large structures is initially controlled by coating systems but due to process upsets the chemistry of the effluent is subject to rapid changes. The opportunities for coating refurbishment are restricted to mill shutdowns at which time (weather permitting) both surface preparation and coating must be accomplished. Often coating integrity assessment cannot be made before dewatering adding to the complication of material and labour estimating.

Cathodic protection achieved by a properly designed system can be installed during operation of the clarifier and can provide an automatic response to process upsets ensuring continuous protection of all immersed surfaces. Cathodic protection takes advantage of the existing coating system while preventing loss of metal at areas where coating damage has occurred. Figure (7) shows the general arrangement of a cathodic protection system mounted in an effluent clarifier. The application of cathodic protection to an effluent clarifier is discussed in detail by Munro [2].



CATHODIC PROTECTION TO EFFLUENT CLARIFIER

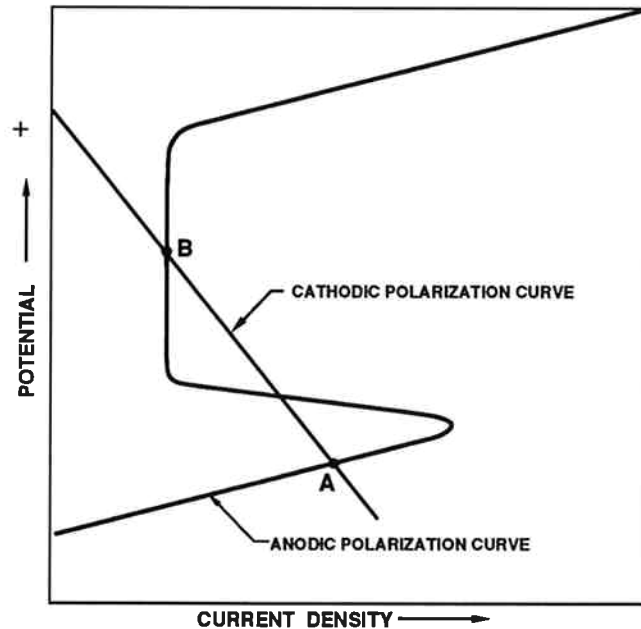
FIGURE 7

The Cathodic Protection current source consists of a rectified DC supply with a controlled current output responding to the potential of the steel structure under protection. The anodes are typically platinized niobium and reference electrodes are liquid junction silver-silver chloride. More than one reference is employed and automatic selection can be provided to ensure that the correct reference is used for feedback control. Provision is usually made for all operating parameters on the system to be transmitted to the plant control room for effective monitoring.

### Anodic Protection

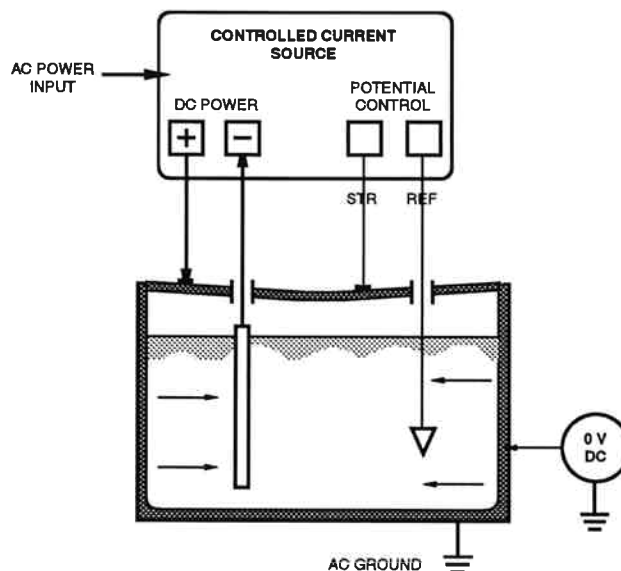
Anodic protection covers the situation shown in Figure (3) where the structure or vessel would be in the corrosion (active) region of potentials either periodically or all the time unless forced into passivity by the discharge of current from its immersed surfaces. Figure (8) shows a theoretical polarization diagram in which there is both an active A and a passive B intercept between the cathodic and anodic polarization curves. Either location will represent a stable operating potential for a corroding system. (Corrosion theory indicates that anodic current must equal cathodic current.)





**FIGURE 8**

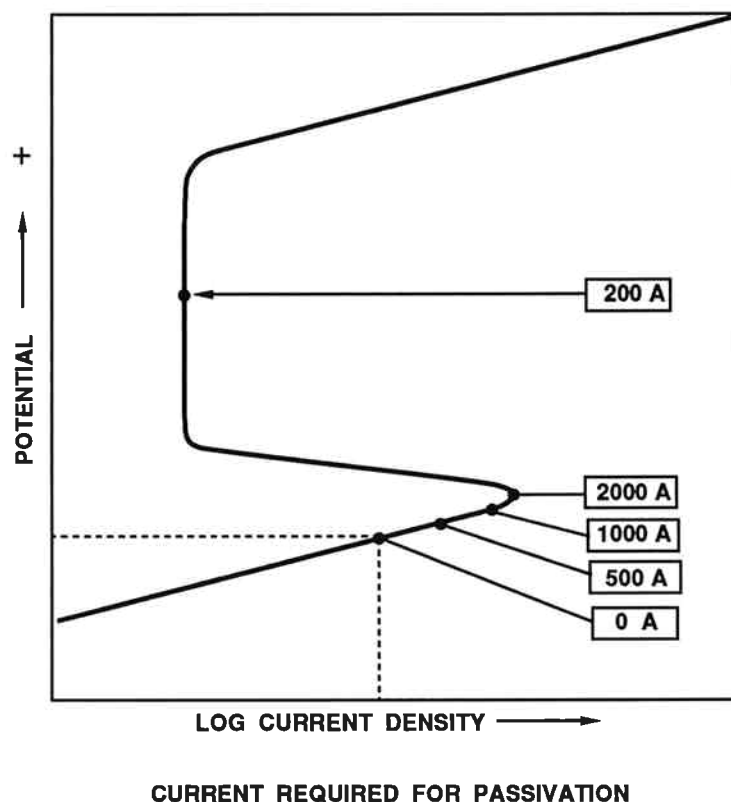
Conceptually an anodic protection system consists of a direct current power supply with its output controlled through a feedback loop that can sense the solution potential of the protected surface. Difference in potential between an internal set potential and the measured solution potential (called an error potential) is amplified and used to adjust the current output of the power supply in such a manner as to reduce the error signal to zero. A simplified illustration of such a system as shown in Figure (9).



**CONCEPTUAL ANODIC PROTECTION SYSTEM**

**FIGURE 9**

Batch digesters using either sulphate or soda liquor become active during the fill and operate for about half the cooking time at potential A after which the digester potential spontaneously swings to intercept B where it remains until the digester is blown. Using an external power source it is possible to force the internal immersed surfaces of the vessel to shift from position A to position B by the discharge of large amounts of current from the digester surfaces to the electrolyte. The path from A to B follows the anodic polarization curve over the “hump” and down into the valley of passivation. As indicated previously the reduction in corrosion rate often exceeds an order of magnitude. In the case of batch digesters, power supplies have to be capable of supplying large currents to achieve initial passivation. Typical current requirements to achieve initial passivation and to hold the digester in the passive zone are shown in Figure (10).



**FIGURE 10**

The initial suggestion that anodic protection would be applicable to sulphate batch digesters was made by W.A. Mueller [3] of Pulp and Paper Research Institute of Canada which led to mill trials in 1958. Large, reliable, controlled DC power supplies were not readily available and several changes in power supplies and cathode design took place during two or three years of experimental activity. Reference electrodes were also developed to achieve the required longev-

ity and accuracy. Feedback control had not yet become available for 3000 ampere power supplies so control was accomplished by timers and contactors related to mill cooking procedures. Watson [4] reported field data on an anodically protected digester in 1964 and proclaimed this technology a practical success. He cited a seven fold decrease in corrosion loss in an operating digester. The Kamyr continuous cooking process was coming into vogue and batch cooking was phased out in many of the older mills. This delayed the application of anodic protection as an effective way of reducing corrosion in these vessels. Weld overlay with stainless steels was actively promoted as a method of upgrading the corrosion performance of mild steel digesters. This was a concept more easily understood by mill management than anodic protection and even at a cost in excess of five times that of an installed anodic protection system was chosen as an alternative method of digester life extension. Annual maintenance charges even on clad vessels usually exceeded the cost of an anodic protection installation.

In the application of this technology to a digester, the original concept included a mild steel pipe cathode centrally supported in the digester by teflon insulated supports attached to the digester wall. Since this electrode was a cathode, it could be sized such that it would be cathodically protected while collecting the current required to maintain the vessel in the passive zone. In the earliest experiments the reference electrode was an Ingruber [5] design developed and patented by Pulp and Paper Research Institute of Canada which was a nitrogen pressurized water cooled calomel reference which contacted the pulping liquor during the cook. This was changed for a simpler version, also calomel, with an asbestos packed teflon bridge introduced into the digester through pressure fittings.

Early studies on the corrosion behaviour of the digesters was undertaken by T.A.P.P.I. who issued a 10-Year Summary of Alkaline Digester Corrosion and Stainless Steel Overlay Experience. The mill average corrosion rate for these digesters was 32 mils per year with a critical area rate of 59 mils/year. Only digesters with less than 900 sq.ft. of stainless steel overlay were included. After 1966 data was gathered on continuous digesters which during a four year period reported negligible corrosion. Where readings were given they ranged from 10–83 mils/year with an average of about 30 mils/year. The continuous digesters did not cycle like the batch digesters and presumably were not subject to the activation of the metal surfaces during the fill that was thought to be responsible for the high rate of corrosion of the batch digesters. Bennet [6] reported serious corrosion in a soda process continuous digester and opted for an anodic protection system. He reported “Compared to all the other alternatives considered to protect the upper zone of the digester from further debilitating corrosion, anodic protection has proven to be the most cost effective measure”.

The general arrangement of the components of an anodic protection system in a continuous digester is shown in Figure 11.

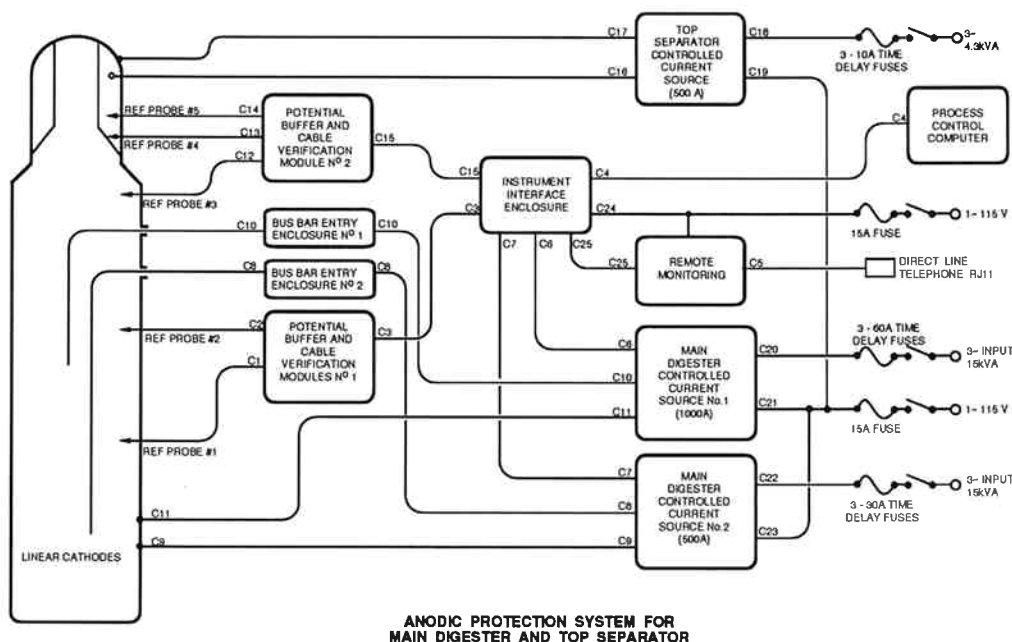


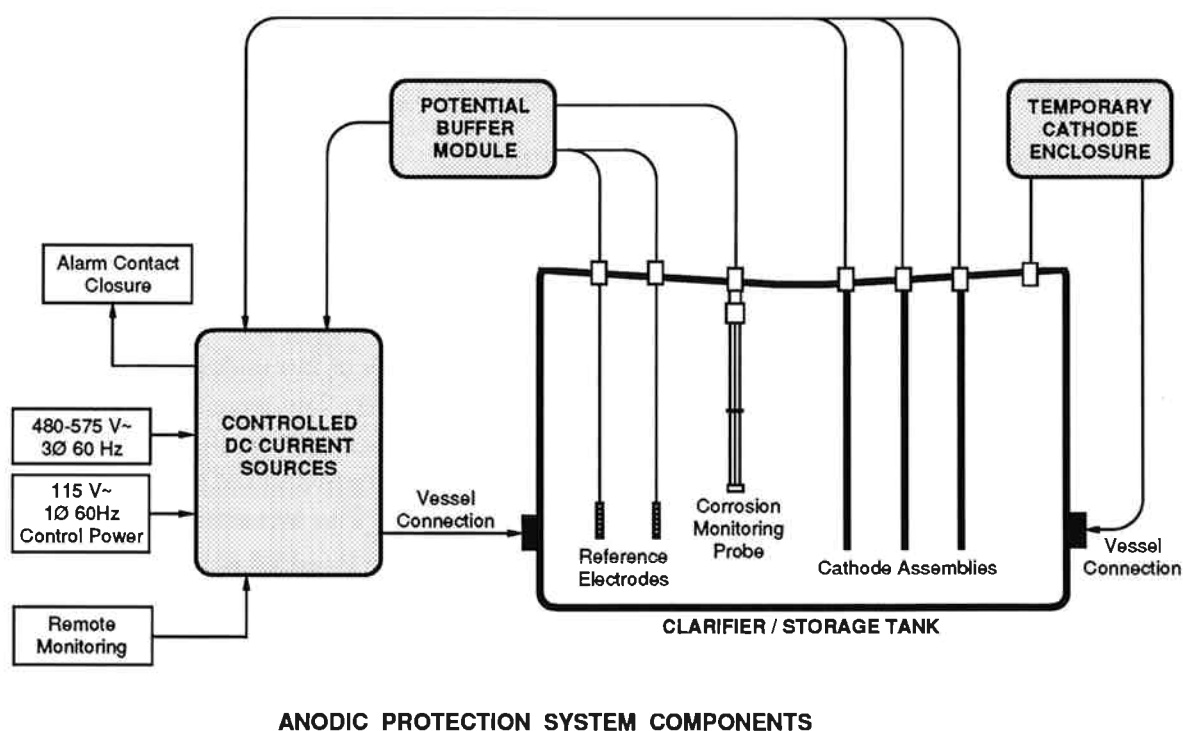
FIGURE 11

Depending on the pulping liquor composition various metals have been tried as control electrodes. These metals usually display a poor temperature coefficient but under the controlled cooking temperature prevailing this is not necessarily detrimental. The measuring electrodes can be changed under operating conditions and sufficient entries are usually available for comparisons to be made. References have buffer-driver units between them and the control room displays or the error amplifiers controlling the DC power supplies. The insulated vessel entry of conductors required to handle the sometimes substantial currents required to passivate an activated digester (say after acid cleaning), requires engineering ingenuity since these entries have to meet pressure vessel insurers code requirements. Anodic protection in alkaline digesters will not only reduce corrosion but it will also prevent stress corrosion crack initiation and propagation. This will be referred to in the discussion on Protection by Potential Adjustment.

### Anodic Protection Applied to White Liquor Storage Tanks and Clarifiers

Deterioration of white liquor tankage "remains one of the most chronic corrosion problems in the pulp and paper industry". [7] Anodic protection was applied to a clarifier in a paper mill in the U.S. by Yeske [8] of the Institute of Paper Chemistry. His laboratory investigation of corrosion rates of mild steel in simulated white liquor was as high as 50 mils per year which could be reduced by anodic protection to a few mils/yr. The current densities required to maintain passivity were in the order of  $100\mu\text{A}/\text{cm}^2$ . Polarization curves performed in the field using clean steel coupons indicated currents required for initial passivation were of the order of  $10\text{mA}/\text{cm}^2$ . The

target vessel had a wetted area of  $5 \times 10^6 \text{ cm}^2$  hence requiring a passivating current of about 50,000 amperes. Coupons were aged in the white liquor for several months and slow step wise polarization curves were generated limiting the current density change of each step to  $0.2 \text{ mA/cm}^2$ . The curve thus generated showed a reduction of current required for initial passivation by a factor of ten with a similar reduction in holding current. Thus encouraged a protection system was designed and installed and after some anticipated startup difficulties is now in successful continuous operation. The Institute reported a ten-fold reduction in corrosion rate with installed cost “a fraction of the cost of a new vessel” and negligible power costs. The general arrangement of the components of this installation is shown below in Figure 12.



**FIGURE 12**

In this application eight cathodes were installed which were suspended from the roof. The controlled current source could deliver 2000 amperes. The passivation potential was in the order of +40mV to a Silver Silver Sulphide Electrode. Yeske indicated that this technology could be successfully applied to green liquor storage tanks and clarifiers. Since this original application many white and green liquor storage facilities and clarifiers have been anodically protected.

## Protection by Potential Adjustment

Examination of Figure 4 indicates that the operation of a normally passive system near either the positive or negative boundaries of the passive region could under some circumstances lead to problems. Increase in the amount of oxidant in a system in which stainless steel is passive will move the potential of the stainless steel in the positive direction. If the potential reaches the point where the anodic polarization curve begins to bend this is usually indicative of the beginning of passive film breakdown and the existence of many small active sites in a passive “sea”. Because of the large potential difference between active and passive stainless steel rapid pitting of the active sites occur, stimulated by the galvanic potential and poor anode cathode area relationships that exist. If one were to apply current to this pitting surface the potential would shift in the negative or cathodic direction until repassivation occurred. If the oxidant level persisted of course the application of cathodic current would have to continue. This application of cathodic current by no means achieves cathodic protection. This region of immunity is on the negative side of the active corrosion zone as Pourbaix’s diagram shows.

In a similar way as discussed by Singbeil [9] sulphate digesters sometimes operate in a range of potentials at the negative boundary of the passive zone and safely into the middle of the passive zone and an anodic current is required to move the potential of the vessel out of this dangerous cracking zone safely into the middle of the passive zone and hold it there if necessary. Again this application of anodic current cannot be construed as anodic protection since we did not have to go over the “hump” of the active passive transition. These two techniques are indeed best called ‘Potential Adjustments’.

## Bleach Plant Washers

Corrosion problems in the pulp and paper industry have been solved by the progressive substitution of more corrosion resistant materials to replace those that have failed due to corrosion. Mild steel is replaced by stainless steel. Stainless steels are often upgraded to more highly alloyed types or replaced with plastic resin composites. Although stainless steels usually perform well in oxidizing environments many problems arose in the bleach plant washers. The workhorse stainless steels of the paper industry, 304 and 316, suffered from crevice corrosion. This led to the substitution of higher alloyed stainless steels containing increasing molybdenum additions such as 317, 904 and 254 SMO for 316. The corrosion problems became much more severe due to the “closing up” of the wash water systems to reduce the impact on the environment. This “closing up” increased chloride concentrations, lowered pH and increased the conductivity of the wash water, changes known to adversely affect the corrosion rate. Figure 13 shows the various potential ranges in which some washers operate related to an anodic polarization curve.

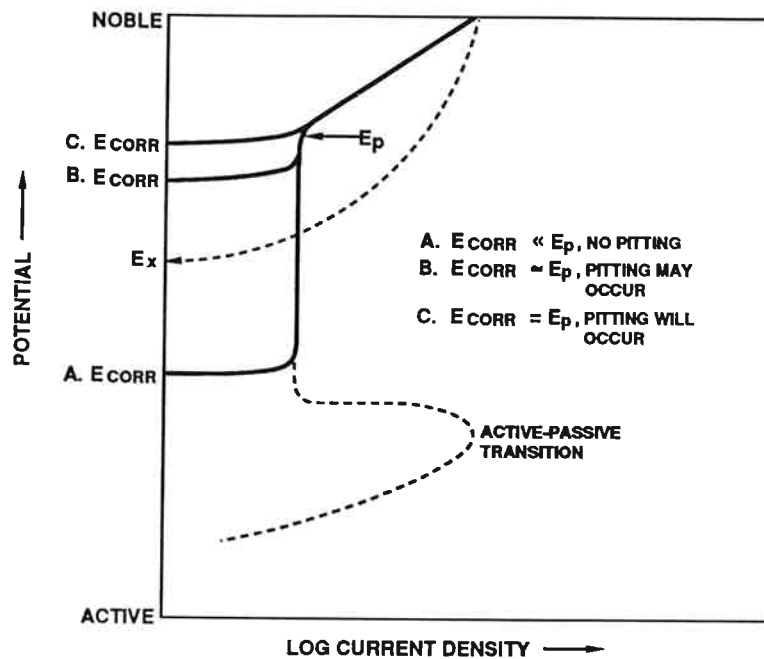


FIGURE 13

Figure 14 shows the effect of increasing chloride concentration. The most significant effect is the movement of the boundary at which pitting commences " $E_p$ " in the negative direction.

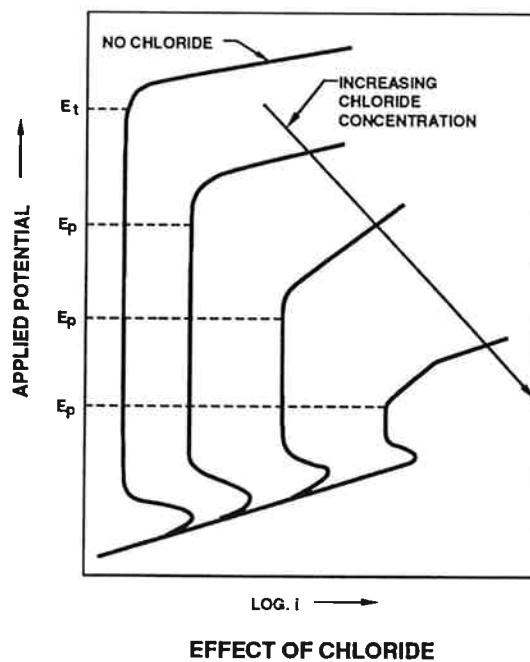


FIGURE 14

Electrochemists were aware that increased oxidizing power in a solution tended to shift the potential of the stainless steels in the positive direction, thus bleach plant washers operating at high chloride residuals were vulnerable to even minor increases of oxidant levels. Increasing the percent molybdenum in the stainless steels pushed the boundary between the passivity and pitting ranges in the positive direction, as shown in Figure 15.

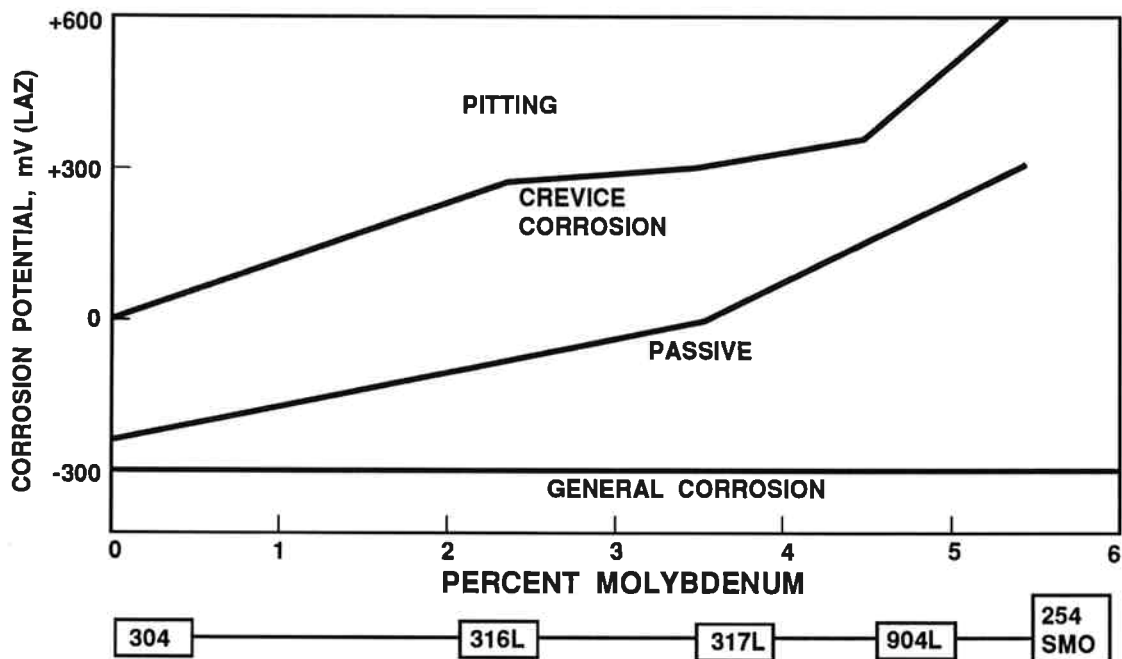


FIGURE 15

The Canadian Pulp and Paper Research Institute [11] undertook a thorough investigation of bleach plant corrosion and set up mill tests in which they effectively reduced corrosion on an operating drum using a potentiostatically controlled rectifier to maintain the drum potentials at an optimum setting. This work resulted in a proprietary system\* for the electrochemical protection of bleach plant washers. Figure 16 shows the effect on drum potentials with increasing chlorine residuals.

\*Process patents held by Canadian Pulp and Paper Research Institute



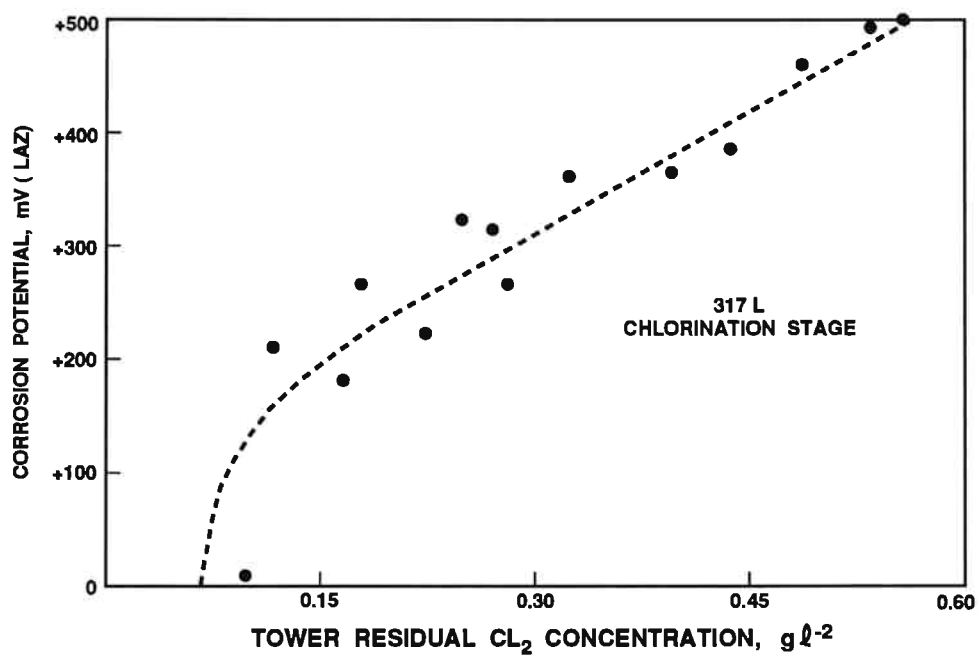


FIGURE 16

Figure 17 shows how the current demand to maintain the “set” potential also increases with chlorine residual concentration.

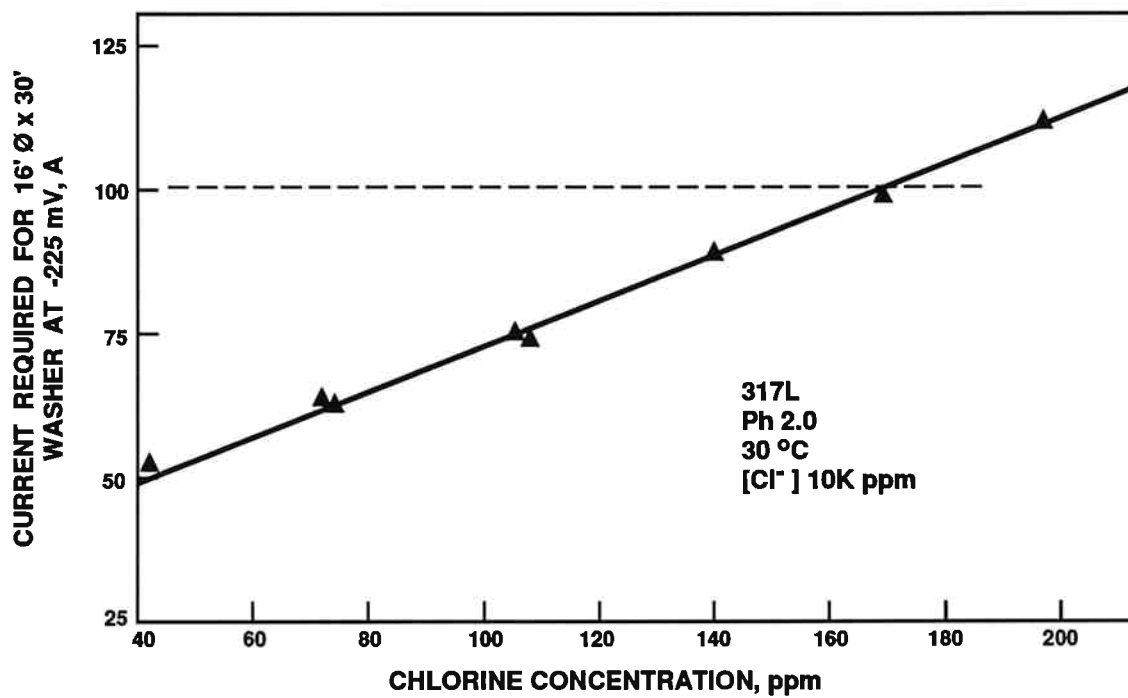
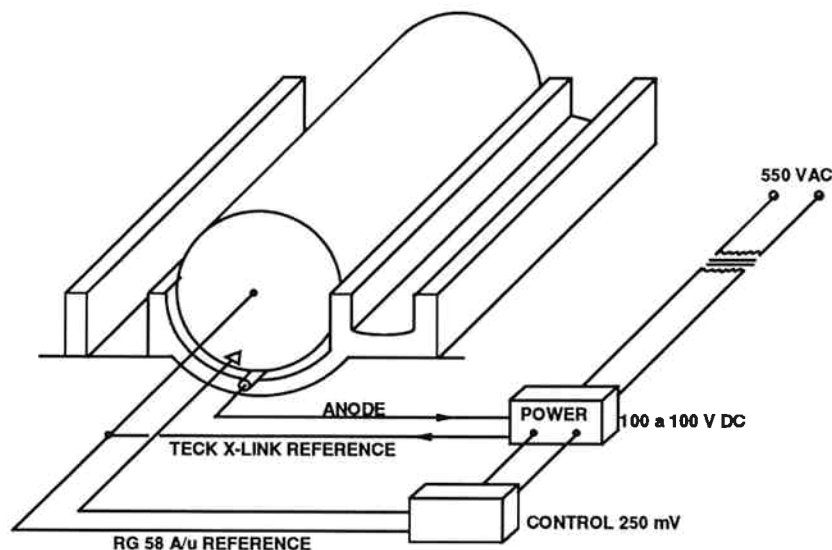


FIGURE 17

Figure 18 shows the basic electrical layout of a protection system on a bleach plant washer. A rectifier unit has its output voltage controlled by an error amplifier that compares the drum potential, measured to a suitable reference electrode, with a "set" potential adjusted to the optimum potential value. The control unit will adjust the rectifier output to reduce the error signal to zero.

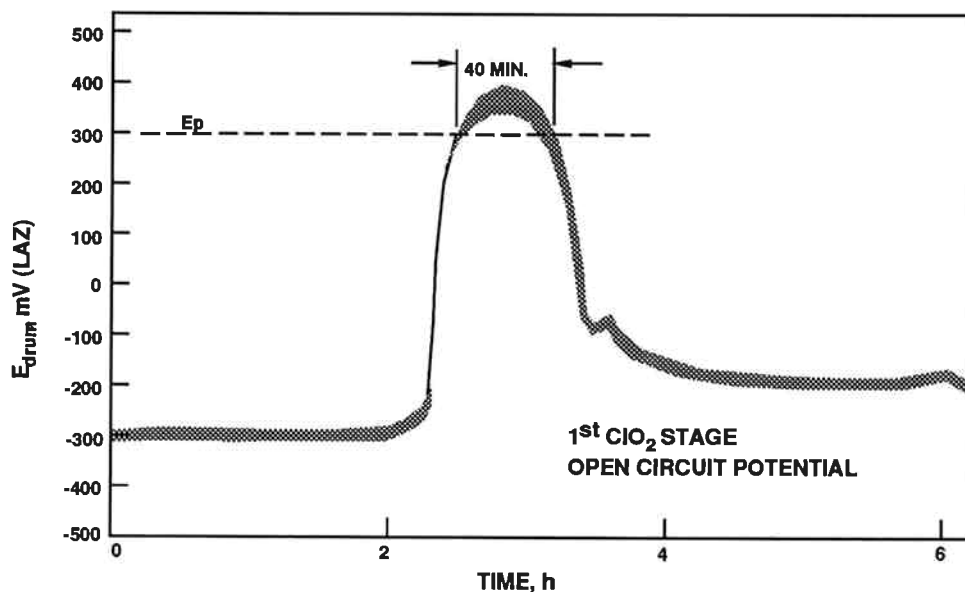


**BASIC ELECTRICAL SCHEMATIC**

**FIGURE 18**

Figure 19 shows a typical potential excursion on a washer drum due to increase in oxidant concentration. Note that the drum potential in this instance remained more positive than the pitting potential  $E_p$  for 40 minutes.

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**FIGURE 19**

Figure 20 shows the effects of operation of potential control equipment on the washer drum potentials. Each previous potential excursion now becomes a current demand which keeps the potential of the drum at or near the set point.

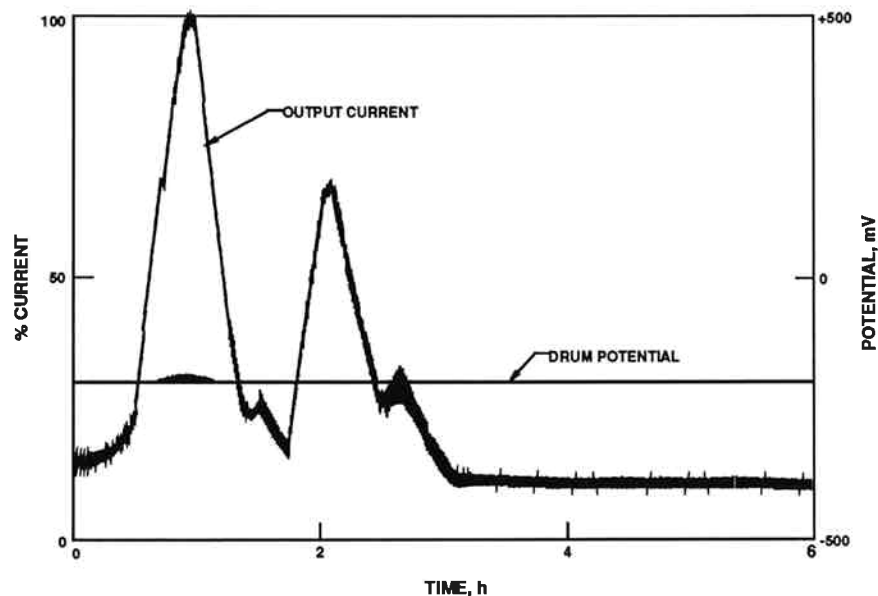


FIGURE 20

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The application of this innovative electrochemical technique increases the life of a washer drum without the necessity of going to more expensive grades of stainless steel.

Laliberté and Garner did an economic evaluation of electrochemical protection on bleach plant washers. They indicated on the basis of data available as of that date (1980) that it was not unrealistic to expect the life of a washer to be doubled by the use of electrochemical protection. Their calculations did not include any maintenance or downtime costs. Where  $\text{SO}_2$  and NaOH antichlors were in use for corrosion control their elimination would result in cost savings in excess of those capital cost savings they showed in their analysis.

Laliberté [12] updated his evaluation in 1983 and indicated in several scenarios that the payback period would be less than 7 months on the basis of antichlor savings alone. Excluding chemical savings he gave a payback period of less than 8 months on a 317L protected washer. As of now over 100 washers have been protected by electrochemical means, the earliest in 1979.

## **Caustic Stress Corrosion Cracking in Continuous Digesters**

A few years ago stress corrosion cracking occurred in a transition weld in the upper section of a continuous digester resulting in the complete separation of the upper section of the digester while under pressure. An industry wide inspection of these areas in other digesters showed that this problem was not confined to a single mill. In fact cracks were found in 60% of the digesters examined. Research by Singbeil and Tromans [10] discovered an operating potential zone in which caustic cracking would occur in sulphate pulping liquors (see Figure 4). This suggested the possibility of preventing crack initiation by electrochemical methods. TAPPI/IPC Digester Cracking Committee funded research into the cracking problem and P.P.R.I.C. in cooperation with this committee examined the effects of potential adjustment on prevention of stress corrosion cracking. They reported [11] that if potentials of both slow strain rate and fracture mechanics specimens were held at a potential 100mV more positive than the active-passive transition potentials no cracks were initiated. Up until this research was reported there were 3 digesters that were anodically protected to reduce corrosion. Examination of these vessels indicated that they remained crack free in the protected zone. Electrochemical protection has subsequently been installed in digesters that had a history of cracking and the T.A.P.P.I. committee has reported that potential adjustment is an effective method of stopping cracking in continuous sulphate digesters.

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