



ANODIC PROTECTION of KRAFT DIGESTERS

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**MATERIALS
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980 M & M Bldg.
Houston 2, Texas

T. R. B. Watson
*Corrosion Services
Toronto, Ontario
Canada*

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ANODIC PROTECTION of KRAFT DIGESTERS*

Dramatic Lowering of Corrosion Rates

SUMMARY

Describes corrosion problems encountered in kraft digesters used in pulp and paper industry. Explains how anodic protection equipment is used to maintain a passive film on digester shell's interior surfaces during cooking cycles to prevent corrosion. Briefly explains principle of anodic protection. Case history data show dramatic lowering of corrosion rates on one digester. Also gives economic data on installation and operation of anodic system, plus savings from prevention of failures and reduced maintenance.

ANOTHER successful application is described in this article of the rapidly expanding technique of anodic protection. This report deals with kraft digesters in pulp and paper manufacturing.

In the manufacture of sulfate or kraft paper products, the first stage is reduction of wood chips to a pulp of cellulose fibers. This is accomplished by cooking the chips in a large steel digester at a temperature of 350 F for about three hours, in a liquor containing 100 grams per liter sodium hydroxide and 35 grams per liter sodium sulfide. The liquor is very caustic and corrosive.

Digesters are vertical, cylindrical vessels of mild steel with conical bottoms. They are about 50 feet high and 10 feet in diameter with a wall thickness of 1½ to 2 inches.

Digester Corrosion Problems

In the pulp and paper industry, where corrosion is ever present, digester corrosion is one of the most serious problems. Two-inch thick vessels in some mills become unserviceable in ten years and have to be replaced at a cost of \$60,000 or more.

The industry has investigated the problem extensively, but the results have been confusing. Corrosion rates vary widely from mill to mill, and until recently there has been no convincing explanation for such variation. Many means have been tried to alleviate the attack, but the only really effective methods, have necessitated cladding with Inconel or weld overlaying with stainless steels. Weld overlay is widely used and has been reasonably successful but has been far from trouble-free.

The corrosion rate of a mild steel digester depends almost entirely on whether its internal surfaces are electrochemically active or passive. Mild steel in hot alkaline pulping liquor is on the borderline between the active and the passive states.¹⁻³ This explains the wide variation in corrosion rates observed in different mills operating under essentially the same conditions. Minor differences in liquor composition can shift the sensitive equilibrium one way or the other—from serious corrosion to virtual immunity.

Polarization Curve Shows Corrosive Periods

The polarization curve reveals a Flade potential of about -0.9 volt in reference to a saturated calomel electrode and active and passive equilibrium points at about -1.0 and

-0.8 volt, respectively. If, then, a calomel electrode is introduced into a digester and connected to a recorder, the chart will provide a record of surface conditions during a cooking operation.

Figure 1 is such a record, obtained by recording the indications of several reference electrodes installed in different places in an unprotected digester shell during a normal cook. At the end of the cook, the digester is passive, but after the "blow" or discharge of the contents it is refilled with chips and strong, hot liquor which boils on the hot surfaces and removes the passive film.

This is why the worst corrosion is usually found where the incoming white liquor impinges on the shell. As the fill proceeds, boiling ceases, but the steel remains active and corrodes rapidly. About an hour after final temperature is reached, progressive dilution of the liquor through interaction with the chips, changes the surface equilibrium until the digester suddenly becomes passive, and it remains in this state for the rest of the cook.

This means that a digester corrodes only during the first half of each cook. If it were possible to keep it passive the whole time instead of only half the time, it would hardly corrode at all. This is accomplished through anodic protection.

How Passivation Is Achieved

Passivation is accomplished by passing a direct current of several thousand amperes from a set of flexible steel cables through the liquor to the shell. This electrochemically oxidizes the surfaces, forming the passive film and shifting the steel's potential into the passive range. Once it is passive, only a small maintenance current is needed to keep the shell passive.

When the digester goes passive half-way through the cook (see Figure 1), it is because of the oxidizing effect of polysulfides, thiosulfates, and other oxidizing agents in the black liquor. Anodic current just accelerates this passivation by supplying supplementary electrolytic oxidation. Any form of oxidation is equivalent to current. Additions of elemental sulfur to the charge will hasten passivity.⁴ If the liquor charge has a relatively high proportion of black to white liquor, less current is required for passivation because of the presence of oxidizing agents.

★ Revision of paper presented at Western Division Conference, Canadian Region, National Association of Corrosion Engineers, February 12-14, 1964, Edmonton, Alberta, Canada

Weld overlay with stainless steel is successful in controlling digester corrosion only because the passive film on stainless steel is more stable than it is on carbon steel and lasts from cook to cook. It would seem more sensible and far more economical to induce a passive film on carbon steel by controlled electrolysis, to achieve the same result.

Equipment Needed Is Simple

The equipment needed for this anodic protection is simple. The cathodes consist of one to three 1¾-inch flexible steel wire rope cables hanging from the digester's dome at 120 degrees around the vertical axis. The cables reach to the top of the cone and are protected from shorting on the ends by Teflon bumpers. The cable cathodes are introduced through the dome via flanged pipe nipples and are insulated from the digester shell with Teflon gaskets. The current impressed on the cathodes can be from any suitably controlled source of direct current. At least one special saturated calomel electrode is introduced into the digester via a Schedule 80 half-inch pipe welded into the shell. The electrodes are sealed by a high pressure, insulated union.

Anodic protection equipment has been installed on one digester for about three years at the Georgia-Pacific Corporation Mill at Crossett, Arkansas. The experimental equipment consists of a selenium rectifier, controlled by timers and tap switches, which powers three cable cathodes. A continuous record of the operation is maintained, giving current, voltage, and the electrolytic potential of digester surfaces with reference to nine reference electrodes in various parts of the shell. A glance at this chart shows whether the digester is active or passive.

The equipment is operated automatically. When the blow valve opens, the current is shut off, but the digester remains passive during the "blow" until it is activated by the incoming liquor. Some corrosion undoubtedly takes place during the fill, but it has been found impractical to passivate the vessel during the period of "hot plate" boiling. Three minutes after the lid is on the digester, the cables are energized. About 4000 amps are passed for three minutes, then a timer reduces the current to about 2700 amps. This current flows for 12 minutes then is reduced to a maintenance current of about 600 amps.

The high current at the outset (see Figure 2) serves to push the potential

"over the hump" of the polarization curve into the passive range. The intermediate current merely develops the passive film until it is stable. The result of the current flow is immediately apparent on the chart. The period of active corrosion is cut from an hour-and-a-half or more to just a few minutes.

The equipment consumes a maximum of 30 kilowatts during the initial surge, and the average power consumption over the period of the cook is less than 2 kilowatts.

Dramatic Lowering of Corrosion Rates

The dramatic lowering of corrosion rates on digesters is given in Table 1. Results of careful ultrasonic surveys taken over an 11-year-period on five digesters show that the worst corrosion occurs in the cone and in the second course. The maximum average corrosion rates for the cone vary from 73.2 to 56.5 mils per year.

After anodic protection was applied for almost two years on one digester (No. 13 in Table 1), the average corrosion rate over the cone was reduced from 73.2 to 10.7 mpy. In the second course, corrosion was reduced from 46.8 to 1.5 mpy. It is understood, of course, that ultrasonic measurements are subject to some inaccuracy, but all readings on the test digester were taken by the same operator, using the same instrument, and certainly show a significant improvement.

No trouble has been encountered with the cathode cables, and they have shown to be serviceable for at least one year. The reference electrodes last three or four months before they have to be replaced. However, this is merely a matter of unscrewing the old one and replacing with a new one.

The appearance of the digester's internal surfaces verifies the dramatic lowering of corrosion rates. Virtually no corrosion was evident at the last inspection.

Although the readings reported are averaged over each course, there were no local areas of attack. This substantiates the theory which dictates that a digester is either all active or all passive.

Permanent anodic equipment will operate on the potentiostat principle instead of using transformer taps. Only one reference electrode will be installed in the cone. By means of saturable reactors, the current will be regulated automatically so that a pre-set potential in the passive range

T. R. B. Watson

*Corrosion Services
Toronto, Ontario
Canada*

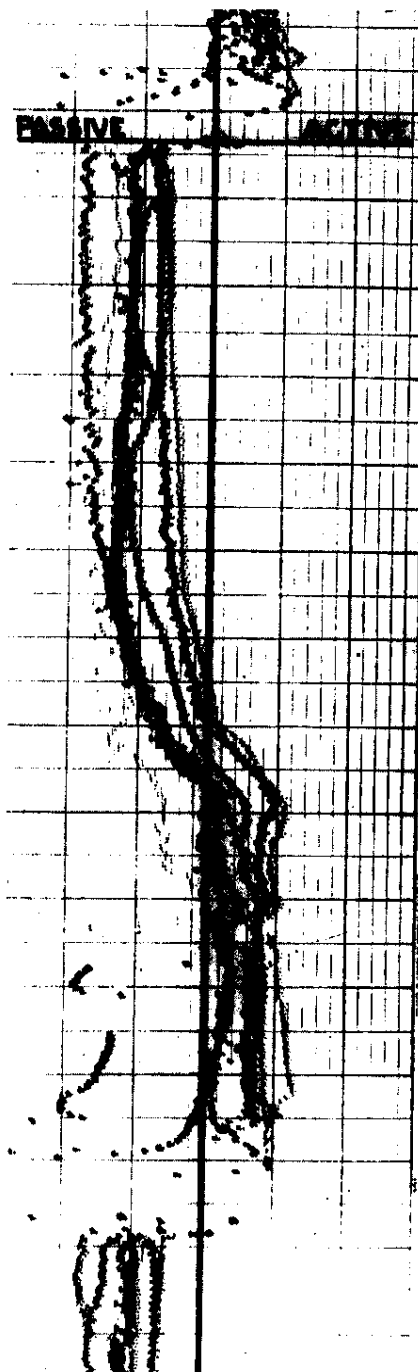


Figure 1—Recorder chart showing potentials of the inner surfaces of a digester during a typical cook. Digester did not have anodic protection. The black line represents the Flade potential at -0.9 volt. Chart speed is 10 minutes per line. Chart shows about half of the cook cycle permits corrosion to occur on the digester shell while it is in the active range.

is maintained. In this way, less power will be used, and the equipment will automatically adjust to unusual cooking procedures.

Overlaid digesters can be protected with far less current than mild steel ones because the passive film is more easily maintained. Anodic protection, in this case, will passivate areas of



Figure 2—Typical chart of digester operation under anodic protection. Traces at extreme left are applied current and voltage. Current is turned off during the blow and fill. Surfaces are active only for 10 minutes during the fill. Chart shows that anodic protection maintains the digester in the passive range during the cook period, thus controlling the corrosion.

dilution or non-coverage. Only one cable cathode will be required.

The capacity of the equipment will vary from mill to mill. The cost of labor, materials, and equipment for anodic protection varies from about \$5,000 to \$10,000 per vessel, depending on the number of units installed and character of the liquor. Yearly

TABLE 1—Corrosion Rates of Digesters, Showing Effect of Anodic Protection*
(Crossett Mill of Georgia Pacific Corporation)

Digester No.	6	7	10	12	13	13
Period of observation (years).....	11.5	10.5	10.6	7.6	6.6	1.66
Protection.....	No protection	No protection	No protection	No protection	No protection	Protected
First course.....	29.8	25.6	30.8	16.8	23.7	No loss
Second course.....	52.8	60.5	49.4	39.5	46.8	1.5
Third course.....	30.7	37.0	40.4	38.2	45.5	5.7
Cone.....	56.5	61.7	70.6	63.3	73.2	10.7

* Corrosion rates are in mils per year and are averaged for each course.

maintenance is about \$500. Cost of electric power is negligible.

At the Crossett mill, it is estimated that if anodic protection can extend the life of digesters sevenfold, as is indicated, savings in depreciation and maintenance will pay for the installation in about two years.

Conclusions

Anodic protection has, in this instance, proved itself to be damatically effective in reducing corrosion losses in an operating alkaline digester. It is economical and relatively trouble-free. There is no doubt that this new method will be widely adopted in the future.

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T. R. B. WATSON, president of NACE, is founder and president of Corrosion Services, Toronto, Ontario, Canada. He has been a member of NACE since 1947 and has been active at all levels of the association. He has a bachelor's degree in applied science (metallurgy) from the University of Toronto. He is a member of TAPPI and is on its Corrosion Committee, is a member of the Engineering Institute of Canada and of the Sea Horse Institute.