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Experience with Anodic Protection of Kraft Digesters

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THIS PAPER reports another successful application in industry of the rapidly expanding science of anodic protection.

In the seven years during which this application has been under development, anodic protection has emerged from the laboratory into industry, where it is now being successfully used in many fields [2—7], notably in the protection of steel tanks containing sulphuric acid and of carbon steel vessels holding highly-corrosive fertilizer solutions.

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 quite widely used, and has been reasonably successful, but has been far from trouble-free.

It is now revealed that the corrosion rate of a mild steel digester depends almost entirely upon whether its internal surfaces are electrochemically active or passive. It has been shown by Mueller [9—11] that mild steel in hot alkaline pulping liquor is on the borderline between the active and the passive states. This explains the observed wide variation in the rate of attack 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.

PRINCIPLE

The basic mechanism of passivity may be studied by plotting the polarization curve, Fig. 1. This is a trace of *current vs. the electro-chemical potential* of a metal specimen immersed in the liquor. The current is that required to maintain the specimen at the given potential. It is seen that, as the potential is made more anodic (more positive), the current required increases exponentially, and, within this potential range, the specimen corrodes rapidly. Suddenly, however, once a certain potential is reached (the Flade potential), the character of the corrosion product changes and the passive film is formed. The resistance of the system increases sharply, and the current drops to almost zero and stays very low throughout a wide potential range. This is the passive range.

The rate of corrosion follows the current throughout these potential changes. As can be expected, the corrosion rate is very hign within the active range, from about 1.0 v. to the Flade potential, -0.9; and there is no appreciable corrosion throughout the passive range. From the shape of the curve, it is obvious that it takes much more current to make a specimen passive than it does to maintain it in the passive range. It is seen also that cathodic protection is possible at potentials more negative than -1.1 v., but that the current required to maintain such protection is inordinately high compared to that required to maintain passivity.

If a specimen is made passive and is then disconnected from any external source of current, its potential will drift back to the passive equilibrium point, which is about -0.8 v. Similarly, any speciment in the active range will, if disconnected, assume a potential which is the active equilibrium point, at about -1.0 v.

This gives us a convenient tool for observing conditions within a digester, because, if a calomel electrode is introduced into the shell and is connected to a recorder and a chart is made for the period of a cook, it will be evident that, whenever the potential is at about -0.8 v., the digester surfaces are passive and are not corroding; but, when the chart shows a potential of about -1.0 v., the digester is active and is corroding rapidly. Figure 2 is such a record, obtained

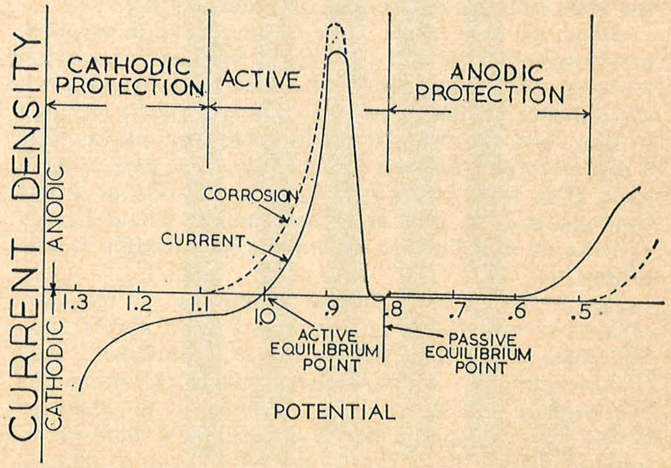

Fig. 1. Idealized form of Mueller's polarization curve.

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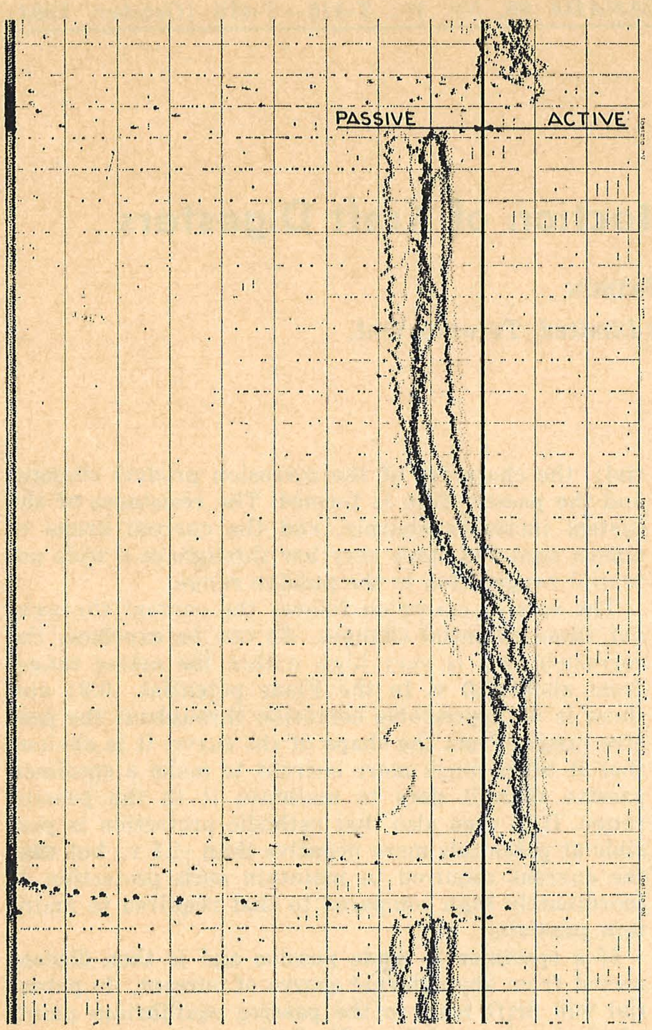

Fig. 2. Record of potential. No protection.

by recording the indications of several reference electrodes installed in different places in a digester shell during a normal cook without protection.

It is seen, that 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.

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 potential of the steel into the passive range. Once it is passive, a small maintenance current is all that is needed to keep it passive.

When the digester goes passive naturally half-way through the cock, it is because of the oxidizing effect of polysulphides, thiosulphates and other oxidizing agents in the black liquor. Anodic current just helps it to do so sooner, by supplying supplementary electrolytic oxidation. Any form of oxidation is equivalent to current. Mueller has shown [12] that additions of elemental sulphur to the charge will hasten passivity. 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.

Weld overlay with stainless steel is successful only because the passive film on stainless steel is more stable than it is on carbon steel, and lasts through 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.

APPLICATION OF THE METHOD

Practically, the equipment is very simple. The cathodes consist of a set of three 1¾-in. flexible steel wire rope cables hanging from the dome at 120 deg. 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

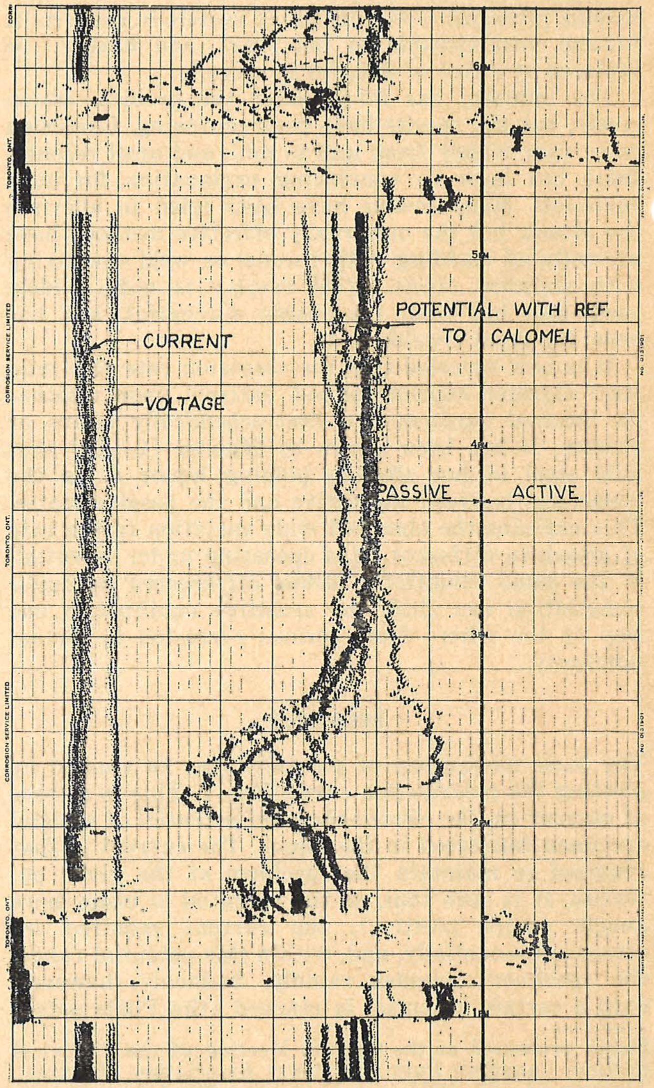

Fig. 3. Record of potential. Anodic protection.

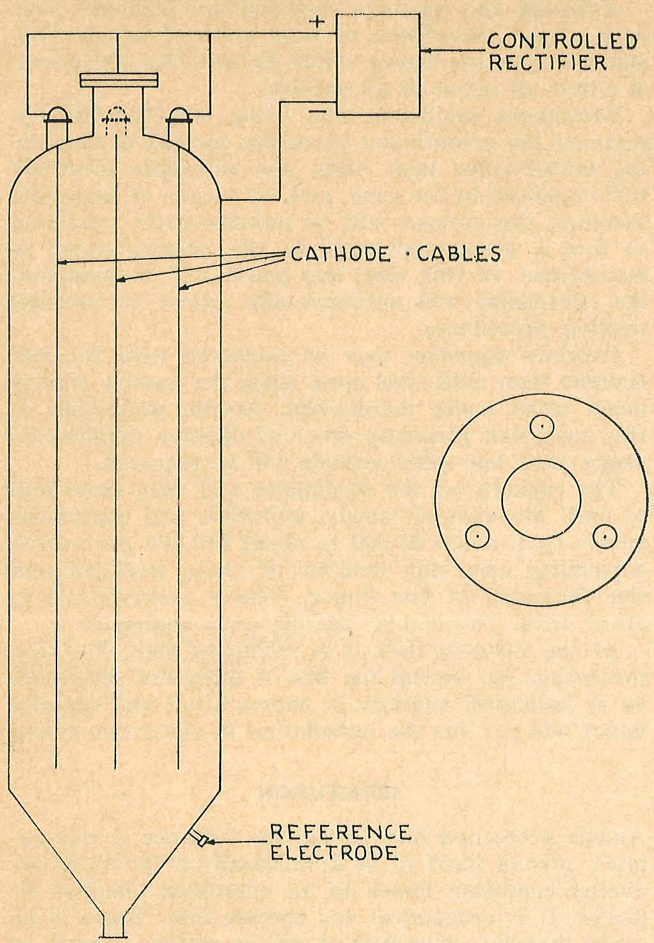

Fig. 4. Arrangement for anodic protection of a digester.

introduced through the dome via flanged pipe nipples, and are insulated with Teflon gaskets. The cathodes are powered by 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, Ark. 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 by a Speedomax recorder, which records 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 cables are energized, and about 4,000 amp. is passed for three minutes, after which a tap-switch timer reduces the current to about 2700 amp. This current flows for a further twelve minutes, after which it is reduced to a maintenance current of about 600 amp.

The high current at the outset, serves to push the potential "over the hump" of the polarization curve into the passive range, and the intermediate current merely develops the passive film until it is stable. The result of the current is immediately apparent on the chart, and the active period is cut from an hour-and-a-half or more to a very few minutes. The equipment consumes a maximum of 30 kw. during the initial surge, and the average power consumption over the period of the cook is less than 2 kw. The results that have been achieved are shown in Table I.

The results of careful audigauge surveys taken oven an eleven-year period on five digesters, including the anodically-protected digester (No. 13), before the installation of the equipment, show that the worst corrosion takes place in the cone and in the second course in every case, and the maximum average corrosion rates for the cone vary from 73.2 to 56.5 mils

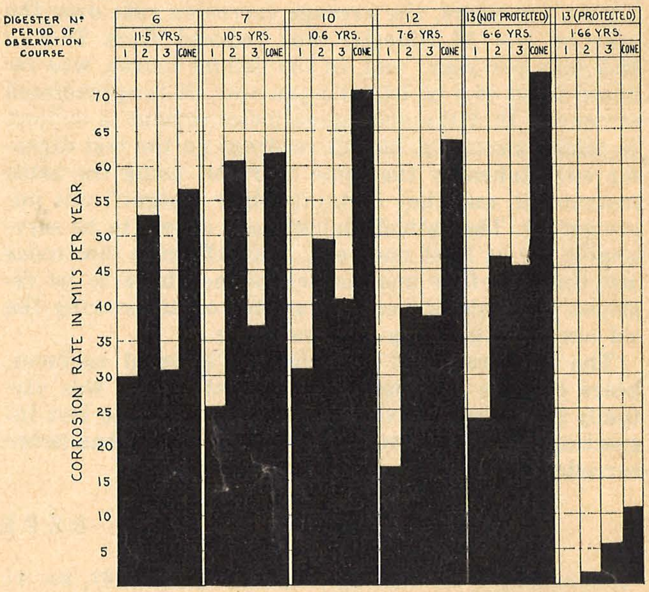

Fig. 5. Digester corrosion rates at Crosset mill.

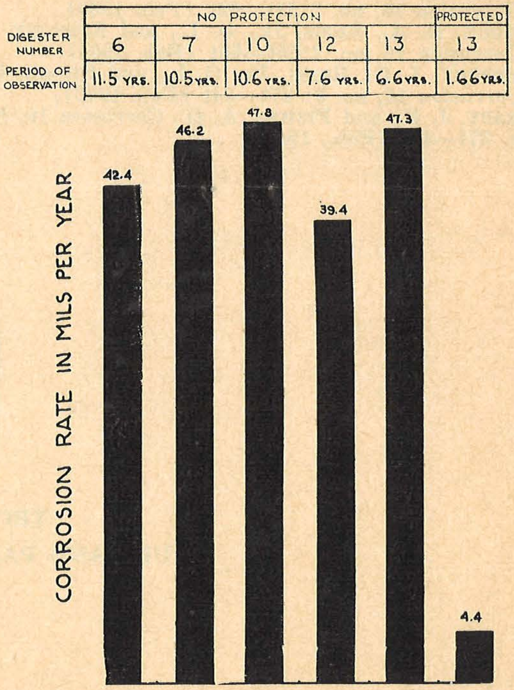

Fig. 6. Average corrosion rates over whole digester.

TABLE I *Corrosion Rates of Digesters at Crossett Mill of Georgia Pacific Corporation. Showing Effect of Anodic Protection.*

Digester No.	*6*	*7*	*10*	*12*	*13*	*13*
Period of observation, yr.	11.5	10.5	10.6	7.6	6.6	1.66
Protection	No	No	No	No	No	Yes
Corrosion rates, mils/yr.						
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

NOTE: Corrosion rates are averaged for each course.

per year. After anodic protection was applied for almost two years, the average corrosion rate over the cone on No. 13 Digester was reduced from 73.2 to 10.7 mils per year; and, in the second course, was reduced from 46.8 to 1.5 mils per year. It is appreciated of course, that the audigauge measurement is subject to some inaccuracy, but all readings on the test digester were taken by the same operator, using the same instrument, and they certainly show a significant improvement. The cathode cables have shown to be serviceable for at least one year. The reference electrodes last three or four months before they have to be replaced, and this is merely a matter of unscrewing the old one and replacing by a new one.

The appearance of the digester internal surfaces, bears out the recorded improvement. There was virtually no corrosion evident at the time of the last inspection. The dome was not attacked, but it has never corroded appreciably in the past.

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 equipment now being installed will operate on the potentiostat principle, instead of employing transformer taps. Only one reference electrode will be placed in the cone, and, by means of saturable reactors, the current will be automatically regulated so that a pre-set potential in the passive range is maintained. In this way, less power will be used and the equipment will automatically adjust to unusual cooking procedures.

Overlaid digesters may be protected with far less current than mild steel ones, since the passive film is much more easily maintained. Anodic protection in this case, will passivate areas of 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 labour, materials and equipment varies from about $5,000 to about $10,000 per vessel, depending upon the number of units installed and the character of the liquor. Yearly maintenance is about $500. The cost of the 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.

CONCLUSION

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

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