Some Recent Advances in Anodic Protection for White and Green Liquor Clarifiers and Storage Tanks

Winston W. Shim, P. Eng.
Corrosion Service Company Limited
Toronto, Canada

Presented at the ABTCP Conference • Brazil, May 2002

Summary

Anodic protection (AP) is a powerful technique for corrosion mitigation of white and green liquor tankage. Recent improvements are discussed. The use of Distributed Current Sources (DCS) resulted in decrease of: 1) mill personnel involvement; 2) logistical hurdles for repassivation, and 3) DC cabling costs. Current distribution design for AP system is critical and it must be based on primary current distribution. The liquor electrochemistry does not allow secondary or higher order current distribution design. Remote monitoring is an integral AP component ensuring that no active areas are allowed to exist in the tank. Full-length corrosion coupons are used to monitor the effectiveness of AP. Care must be exercised to ensure erroneous coupon results due to the effects of low resistivity liquor are minimized.

A Protecao Anodica (PA) e uma poderosa tecnica para mitigacao da corrosao em tanques de licores branco e verde. Melhorias recentes sao discutidas. O uso de Fontes de Corrente Distribuidas (FCD) resultou na diminuicao de :
1) mao de obra envolvida no processo
2) barreiras para repassivacao
3) custo de cabeamento DC.
O projeto de distribuicao de corrente no sistema de PA e critico e deve ser baseado na distribuicao de corrente inicial. A eletroquimica do licor nao permite projeto com corrente elevada ou secundaria. A Monitoracao Remota e uma componente integral da PA, assegurando nao serem permitidas existencias de areas ativas no tanque. Cupons de corrosao longos sao usados para monitorar a eficacia da PA. Entretanto, cuidados devem ser exercidos para garantir que resultados erroneos devido a efeitos da baixa resistividade sejam minimizados.

Key Words:

Anodic protection, corrosion, kraft pulping, white liquor, green liquor, remote monitoring, coupon corrosion monitoring

Protecao Anodica, corrosao, kraft polpa, licor branco, licor verde, monitoracao remota, monitoracao por cupom de corrosao

Introduction

Kraft pulping uses white liquor for wood delignification in the digester. White liquor consists of NaOH (≈100 g/l) and Na_2S (≈30-45 g/l)[1] in addition to other inorganic and organic components. The spent weak black liquor from the digester is concentrated and sensible heat is recovered via the recovery furnace. Sodium sulphate (Na_2SO_4) is added as a makeup chemical. Dissolving the smelt from recovery furnace forms green liquor which consists mainly of Na_2CO_3 (≈80-100 g/l), NaOH (≈10-30 g/l), and Na_2S (≈40 g/l)[1] at a pH of 10-12. Adding CaO and water to the green liquor completes the recautersizing process where white liquor is the end product. Fig. 1 shows a simplified recaustersizing circuit block diagram.[2]

White and green liquor storage tanks and clarifiers made of carbon steel usually suffer from corrosion with the tidal zone being most problematic area. A corrosion rate of 1.3 mm per year (50 mils per year) is common for an unprotected tank. Based on this corrosion rate, a tank with a 6.3 mm (¼ inch) corrosion allowance will require extensive repairs in 5 years. Anodic protection (AP) is a powerful technique used to decrease the carbon steel tank corrosion rate. A five-time tank life extension to 25 years is achievable when the corrosion rate of protected tanks is lowered to 0.13 mm per year (5 mpy).

Fig. 2 is an idealized polarization curve of white liquor and carbon steel. By applying a controlled positive current, the tank potential is moved from the active to passive zone where corrosion is mitigated. The discussion of basic anodic protection and its application to liquor tankage is covered in other publications.[3,4,5]

Original Anodic Protection Design for White Liquor Clarifier

Corrosion Service's first successful application of AP of liquor tankage was in a white liquor clarifier (WLC) in 1984.[6] Subsequent similar applications in the following decade required DC of up to 4,000 amperes at 12 volts.

AP of white liquor tankage only requires the full 4,000 amperes during initial passivation. The tank potential is moved from the active region (Fig. 2), through the high current demand active/passive transition, and finally it remains in the low current demand passive region where corrosion rate is low. Steady state current requirement could be as low as 200 A. This characteristic and the high costs of controlled current sources led to the design of splitting the 4,000 A source into two 2,000 A sources. The mill used a 2,000 A-12 V source as a permanent installation and another 2,000 A-12 V source is rented temporarily to provide the AP system with a total of 4,000 A. This was a sound strategy with some logistical drawbacks. For example, a rental current source is not always available when required and demands on electricians to relocate wiring can be onerous.

Distributed Current Sources (DCS)

As our company became more vertically integrated, in-house current source design and manufacturing resulted in more economical current supplies. AP systems for larger white liquor tankage are now supplied with a permanent 4,000 ampere controlled current source housed in eight modular 500 A transformer-rectifier (T-R) NEMA 4X enclosures. This modular design allows flexible current design (up to 4,000 A in 500 A increments). Fig. 3 is a schematic of the DCS electrical setup for AP system. The output of each of the 500 A T-R is controlled by a smaller AC feed from the control electronics enclosure. This smaller AC feed to the T-R resulted in significant cabling cost savings.

Large DC requires very expensive heavy cabling (ie, 500 and 600 MCM). This cabling is a significant cost of installing an AP system. The older design had sensitive control electronics in the same enclosure as the T-R component of the current source. The control electronics must be kept in a clean room such as the MCC. As the MCC may be a long distance from the clarifier, this very often resulted in a large quantity of heavy DC cabling requirement.

The DCS design put the control electronics in a separate enclosure. This enclosure remains in the clean room. The less-environmentally sensitive T-R may now be installed on the clarifier roof resulting in significant reduction in DC cabling requirement. See Fig. 4 and 5.

Current Distribution and Remote Monitoring

Design of anodic protection of a liquor tank is based solely on primary current distribution. Primary distribution is based on geometry - spacing between cathodes and tank wall only. Other factors such as liquor resistivity and electrode polarization effects are of importance for the secondary and higher order current distributions but they are not considered in AP design.

In Fig. 2, the “transpassive” zone is often considered as a region where metal oxidation is occurring at high potential. This is not the case for white and green liquor electrochemistry. The “transpassive” zone is due to oxidation of sulfide species in the liquor. Some possible reactions are as follows:

$$2S^{2-} \rightarrow S_2^{2-} + 2e^- \qquad \text{.........(1)}$$

$$S_2^{2-} + S^{2-} \rightarrow S_3^{2-} + 2e^- \qquad \text{.........(2)}$$

As the potential is increased, this sulfide oxidation will consume the AP current and prevent the higher order current distributions from taking place. In other words, the passive wall area will not grow with time. This could result in a situation where active and passive areas co-existing adjacent to each other regardless how much current is used. Corrosion Service liquor AP system designs are based on an even primary current distribution around the tank. The minimum/maximum current ratio on the tank wall is designed to be no less than 0.9. This topic is covered elsewhere.[7,8]

Critical analysis of the potential readings and current source output is necessary to detect active areas in the liquor tanks. Potential and current readings obtained manually or through remote monitoring computers must be reviewed by experienced personnel on a regular basis. A clarifier without actively corroding areas manifests itself with low current output and reference potential readings that are very close to each other. Active areas may be detected via a potential triangulation technique coupled with higher than normal current output. Our remote monitoring algorithm will detect actively corroding areas and automatically triggers the auto-repassivation procedure.

The auto-repassivation procedure is a sub-routine of the data acquisition algorithm of the Remote Monitoring Unit (RMU). The sub-routine triangulates three submerged reference electrodes and determines whether the readings are within a predetermined criterion or not. Permutations of all submerged reference electrodes are evaluated. If one or more of the permutations do not meet the predetermined criterion, the current source outputs its maximum power for a set period of time overriding the current source internal control electronics. This auto-repassivation routine continues to cycle until all reference electrode triangulations meet the predetermined criterion.

Corrosion Coupon Monitoring

Corrosion coupon monitoring may be used as a confirmation that the AP system provides effective corrosion mitigation. The original coupon consisted of two 3.17 mm diameter (1/8 inch) carbon steel wires suspended from the roof to the floor of the clarifier. The full-length coupon was made of multiple lengths of carbon steel wire crimped together with stainless steel butt splices. One coupon was connected to the clarifier roof (via an AWG#22 wire) with AP installed and the other coupon was left isolated as a *control*. The whole assembly was supported by a stainless steel wire and non-metallic fittings located between the two coupons. An advantage of using this type of coupon is that a corrosion profile of the tank wall is obtained. Unfortunately, some coupons had erroneous readings after a 90-day exposure. An investigation was carried out to determine the cause and the analysis is presented below.

White liquor has a low resistivity (1-3 ohm-cm). This low resistivity results in a significant current attenuation effect along the wire. The equation for current attenuation along a wire is:

$$I=I_0(\sinh(\alpha(L-x))/\sinh(\alpha L)) \quad \text{.........(3)}$$

And the current density along the coupon wire is:

$$i=dI/dx= -\alpha I_0(\cosh(\alpha(L-x)/\sinh(\alpha L)) \quad \text{.........(4)}$$

where I is current at x
i is current density at x
I_0 is total current
α is attenuation constant
L is length of coupon
x is any point along the coupon

The constant α is dependant on the relative values of linear resistance of the carbon steel coupon and the bulk liquor resistivity. Under low resistivity liquor conditions, the current attenuation along the 3.17 mm (1/8 inch) wire was significant. The situation was exasperated by the high resistivity crimp fittings that were used to join the coupon wire sections together.

Little or no protective AP current was reaching the far end of the “protected” coupon. In addition, the poorly distributed current along the coupon resulted in certain areas residing in the high corrosion zone at or near the active/passive transition of the polarization curve (Fig. 2).

In Fig. 6, curves based on Equation (4) for various diameter coupons are shown. The x-axis is the distance from the energized end of the coupon and the y-axis is the coupon current density. The simulation used a 1,000 cm long coupon with 10 micro-ohm-cm resistivity (ie, carbon steel) and 3 ohm-cm liquor. The 3.17 mm diameter coupon attenuates 50% of the current density, from 0.6 mA/sq cm to 0.3 mA/sq cm, at a distance of 120 cm. In comparison, the 9.5 mm diameter coupon attenuates to 50% current density at 350 cm. Ideally, the current density curve should be a flat line (“no attenuation” case) but that would involve a very large and cumbersome coupon. In practice, a smaller diameter coupon with some attenuation may be used because a long coupon located in a longitudinal direction with the tank has almost perfect current distribution. Polarization of the coupon will lead to a more even current attenuation profile.

In order to confirm the calculations, two new coupons were installed into a clarifier for testing. One coupon was 9.5 mm (3/8 inch) diameter and the other was 3.17 mm (1/8 inch) diameter. Instead of crimping, full penetration welds were used to join the wires together to make up the full coupon length. Both coupons were connected to the protected clarifier with AP system set at +80 mV potential.

In Fig. 7, the current from the protected tank to the 9.5 mm diameter coupon decreased to near zero value after a few days of exposure. The corresponding potential reading in Fig. 8 confirmed that it achieved the same potential reading as the clarifier. The insitu polarization curve in Fig. 9 indicated potential greater than 0 mV as passive. In contrast, the 3.17 mm diameter coupon current demand decreased but never achieved the protected criterion in 13 days. It remained in the high corrosion potential region.

Figs. 10 and 11 are plots of “protected” and “unprotected” coupon corrosion rates for white and green liquor as measured by a properly designed coupon set. An important result from the coupon test is that significant corrosion protection was achieved in the tidal zone of the clarifier/storage tank. It was believed that the AP current protects the coupon when the coupon was immersed during high liquor level. If the liquor level is lowered, the protective layer remains intact for a significant length of time. Although this protective layer will breakdown eventually, protection is offered during the initial critical period of a wetted surface in vapor zone when corrosion is active.

Conclusions

1) Distributed Current Source (DCS) design offers higher current capacity at an economical cost to the mill. The design also lowers installation costs due to the shorter DC cabling requirements and mill involvement in the maintenance.

2) Anodic Protection (AP) design for liquor tankage is based on primary current distribution. Critical analysis of the potential data ensures that no accelerated corrosion occurs. The installation of an RMU will help to minimize or eliminate this possibility.

3) Corrosion coupon monitoring is an excellent method to measure the effectiveness of anodic protection. The long coupons suspended from the roof to the floor of the tank provide corrosion rates at all elevations. Due to the low resistivity of the liquor, the diameter of the coupons must be sufficient to prevent attenuation of the protection current.

Figures

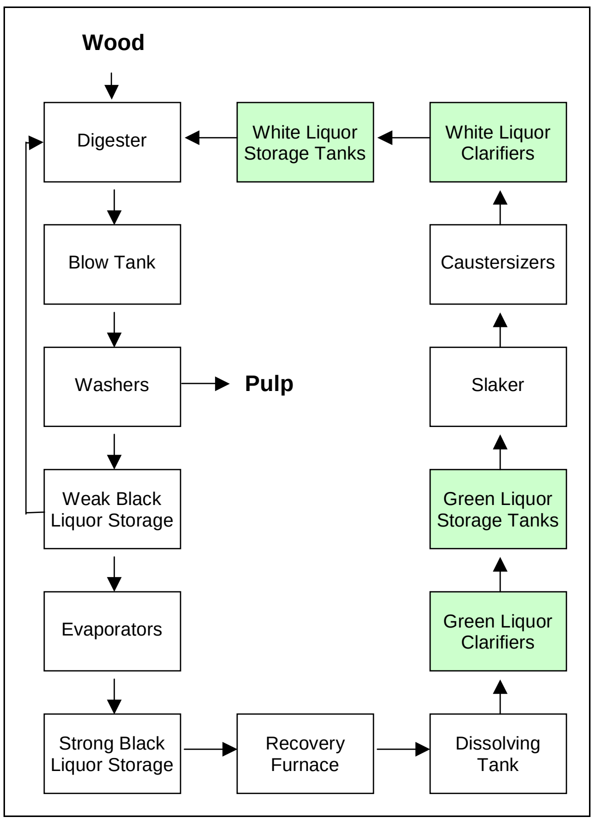


Fig. 1: *Block diagram of kraft pulping and recauster-sizing circuit. Green blocks denote tanks & clarifiers relevant to this paper.*[1]

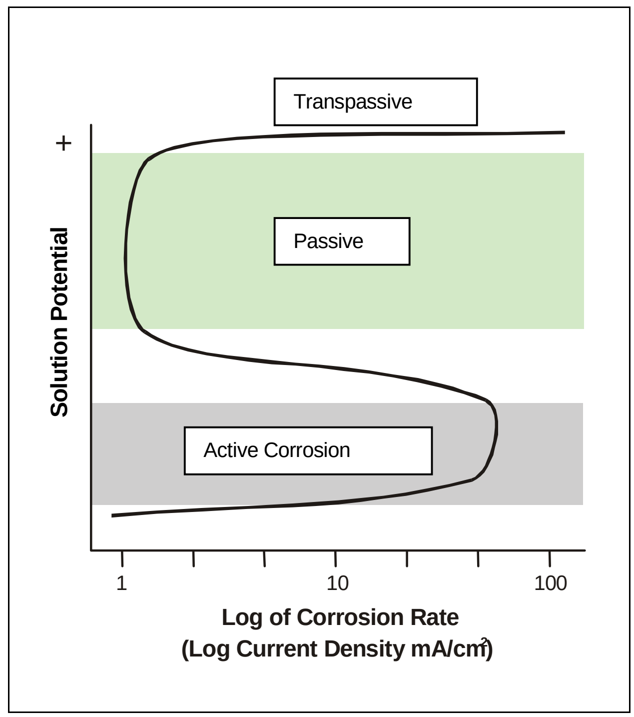
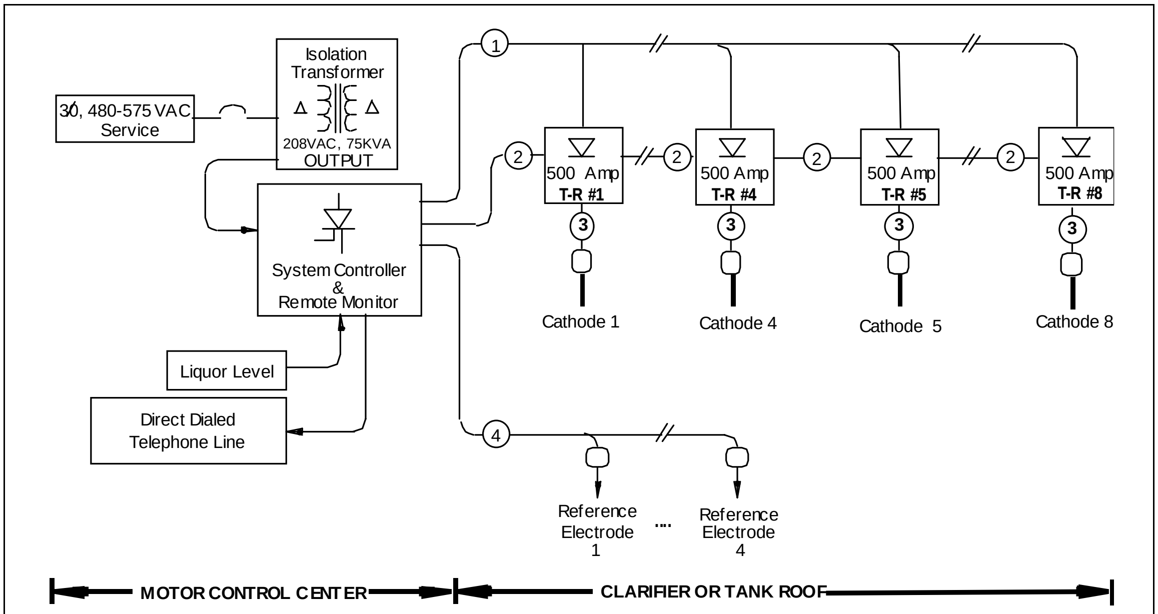


Fig. 2: *Polarization curve showing active/passive behaviour with corrosion zones identified.*



ANODIC PROTECTION SYSTEM ELECTRICAL SCHEMATIC
80 Ft. to 120 Ft. DIAMETER TANKS AND CLARIFIERS

	Function	Cable
1	208 VAC, 3 ph, 100 Amp	4 x AWG 2/0
2	Thermal Interlock	2 x AWG #18
3	0-500 Amp	1 or 2 X 500 or 600 MCM
4	Instrumentation	3 x AWG #18

Fig. 3: *Anodic protection system electrical schematic for white liquor clarifier or storage tank.*

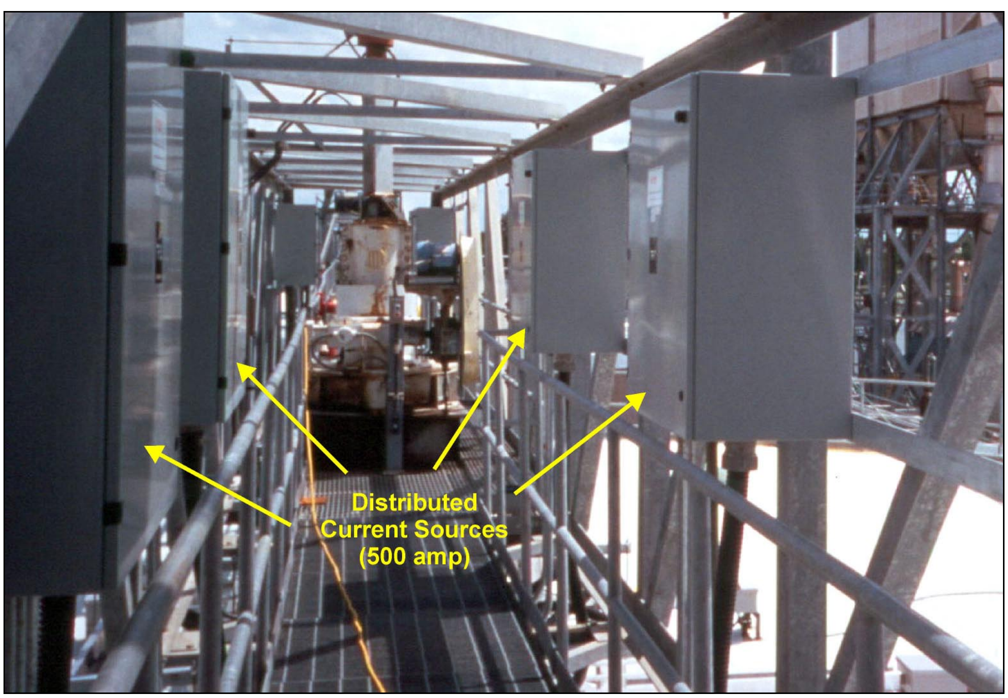


Fig. 4: *Distributed current source arrangement.*

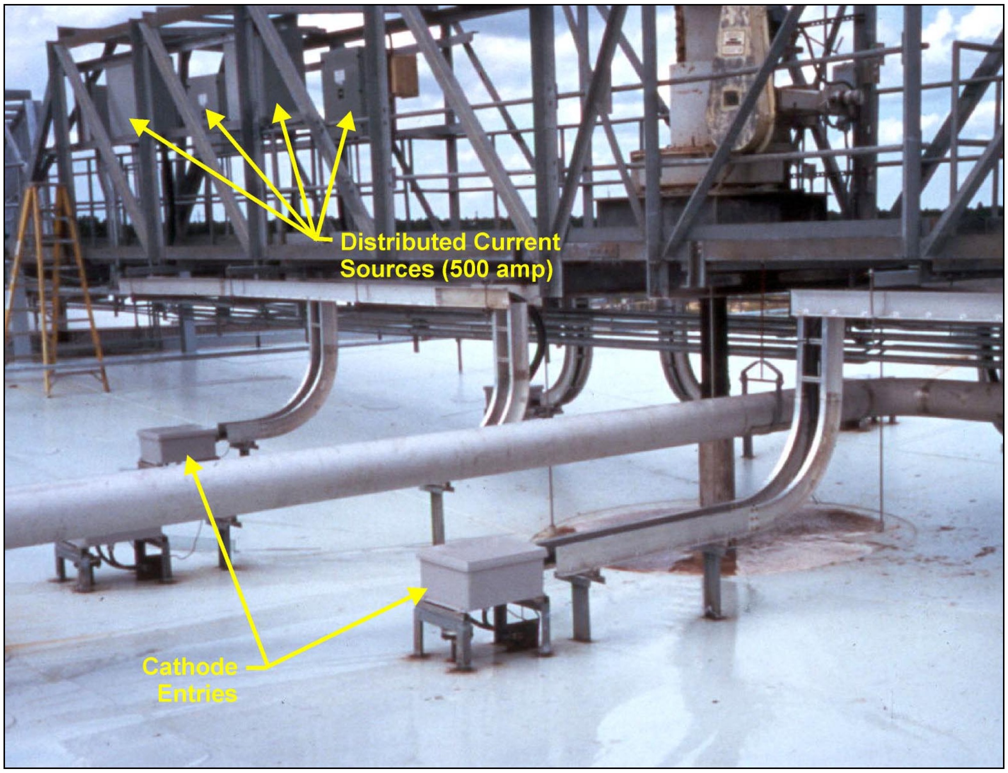


Fig. 5: *Distributed current source arrangement and cathode entries.*

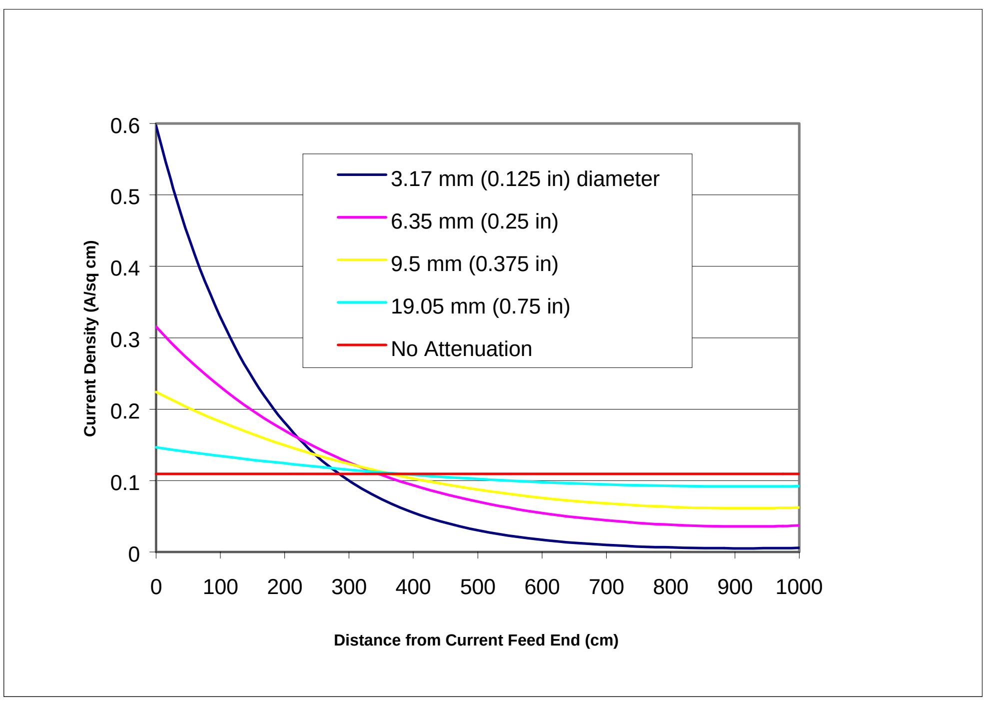


Fig. 6: *Equation (4) attenuation curves for various diameter coupons in 3 ohm-cm liquor.*

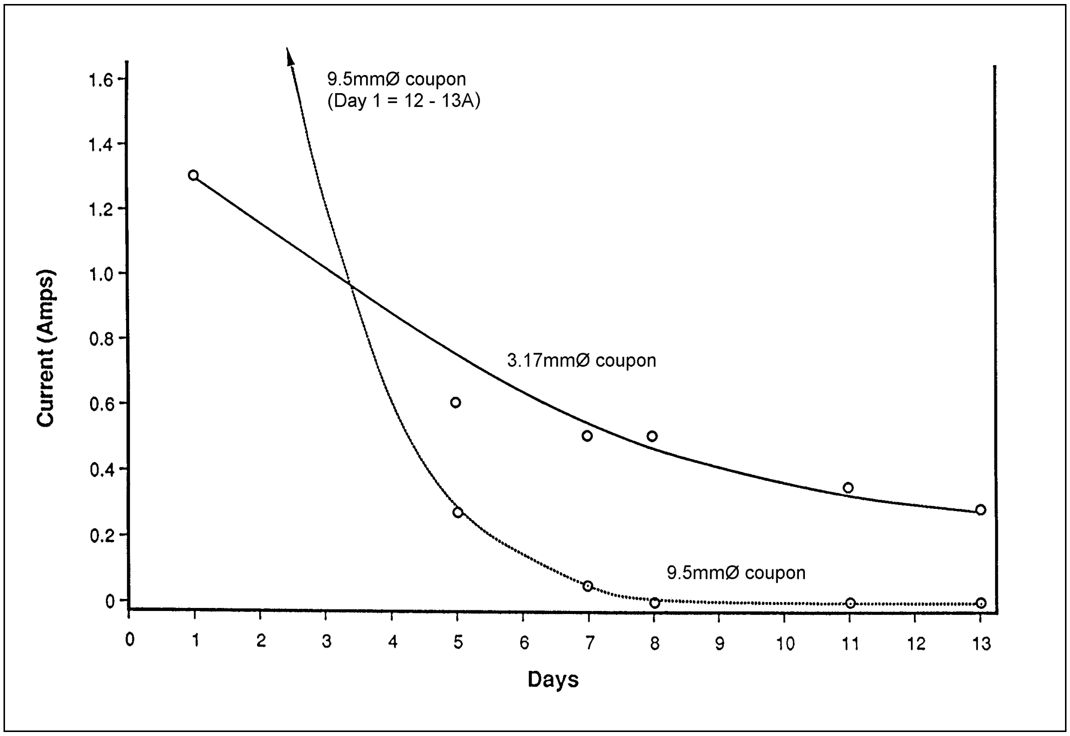


Fig. 7: *Current from clarifier to 9.5mm diameter coupon and 3.17mm diameter coupon as measured by an ammeter in series with the grounding wire of coupons.*

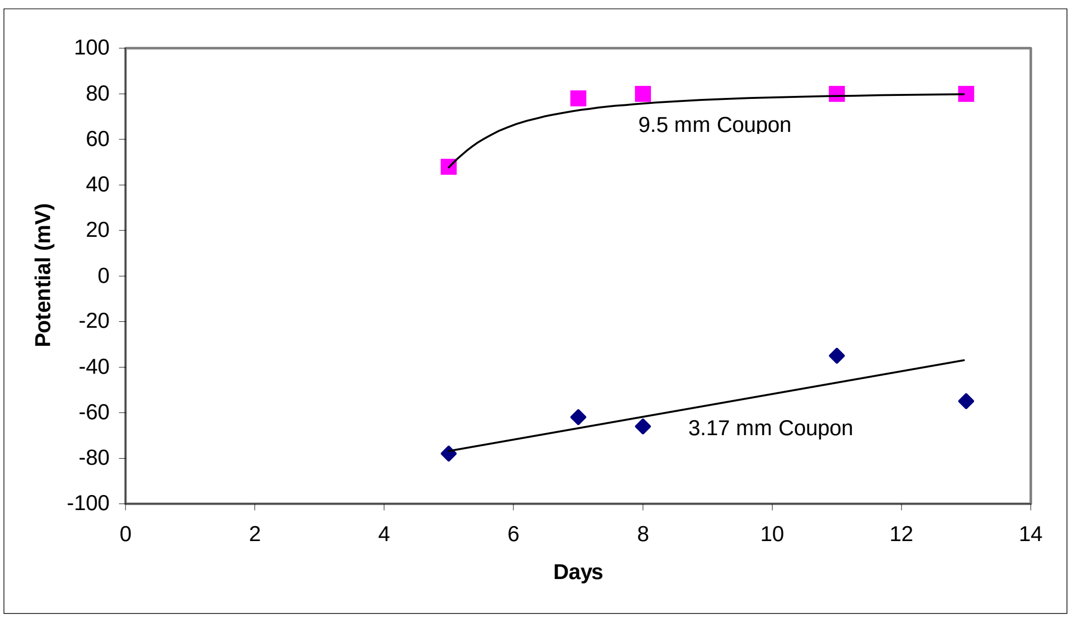


Fig. 8: *Potential readings of 3.17mm diameter & 9.5mm diameter coupons over a 13 day period.*

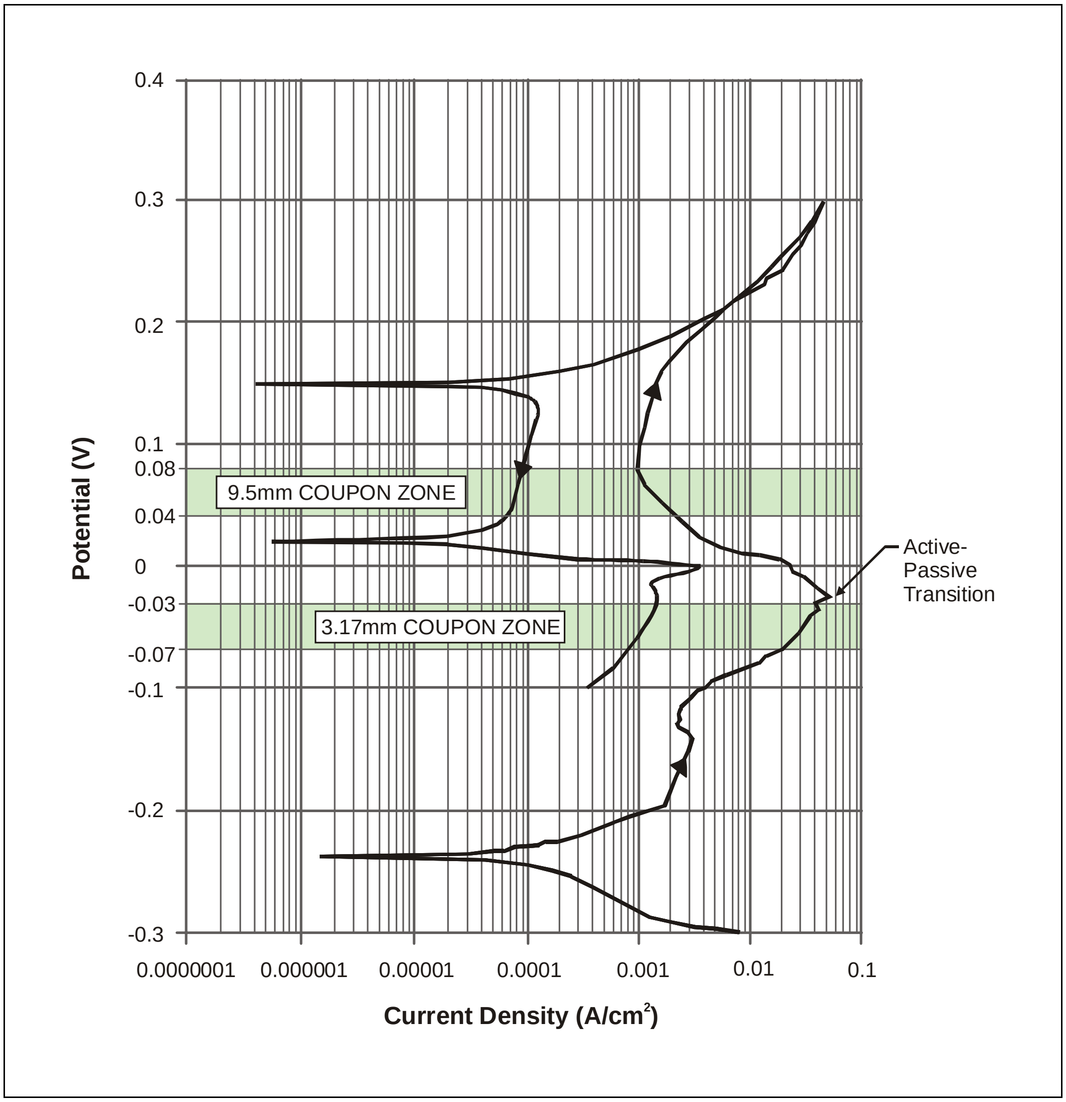


Fig. 9: *Insitu polarization curve of C1018 samples in a white liquor clarifier. Potentials in the coupon zones are highlighted.*

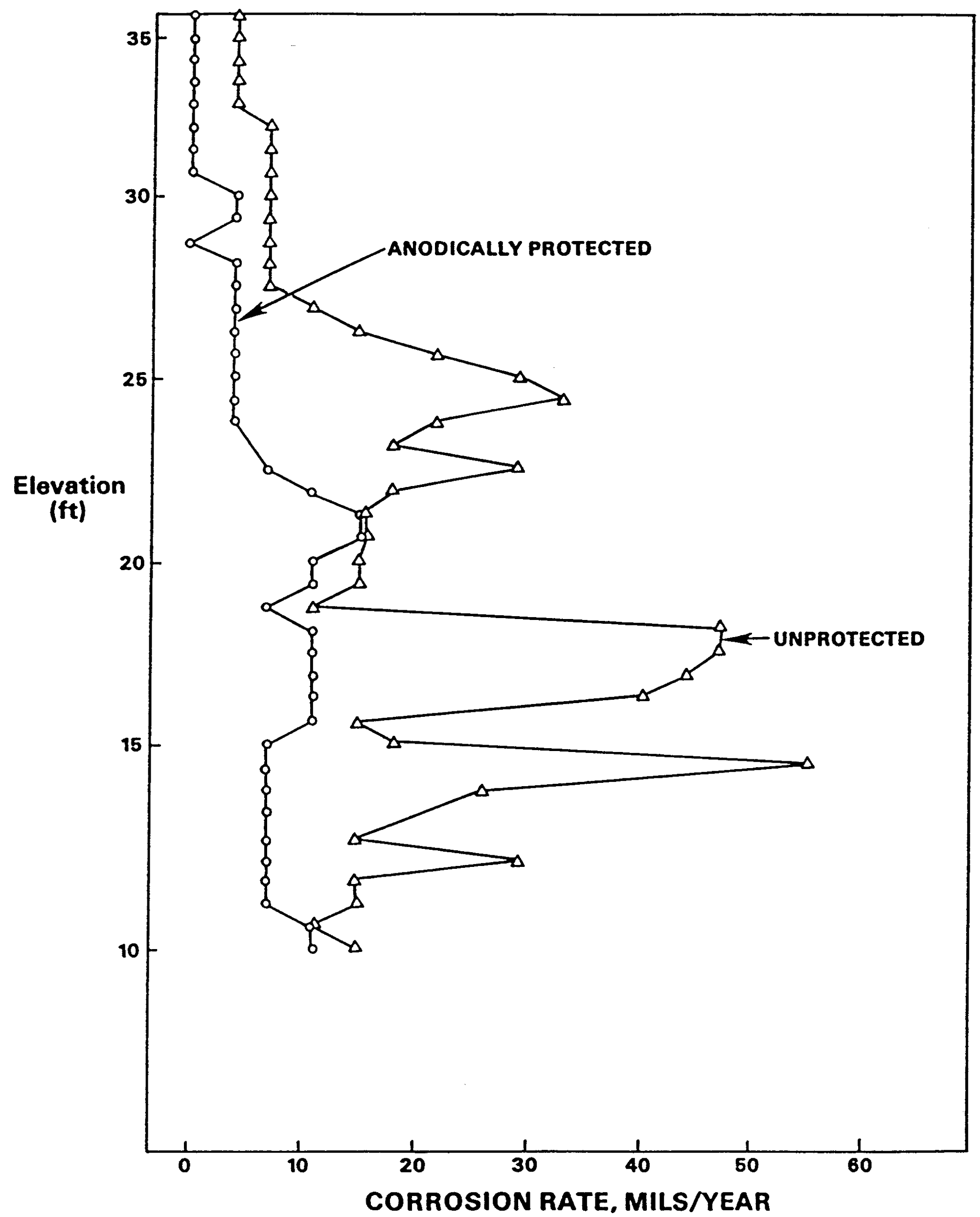


Fig. 10: *Corrosion rates at different elevations on protected and unprotected rods suspended in a white liquor clarifier.*

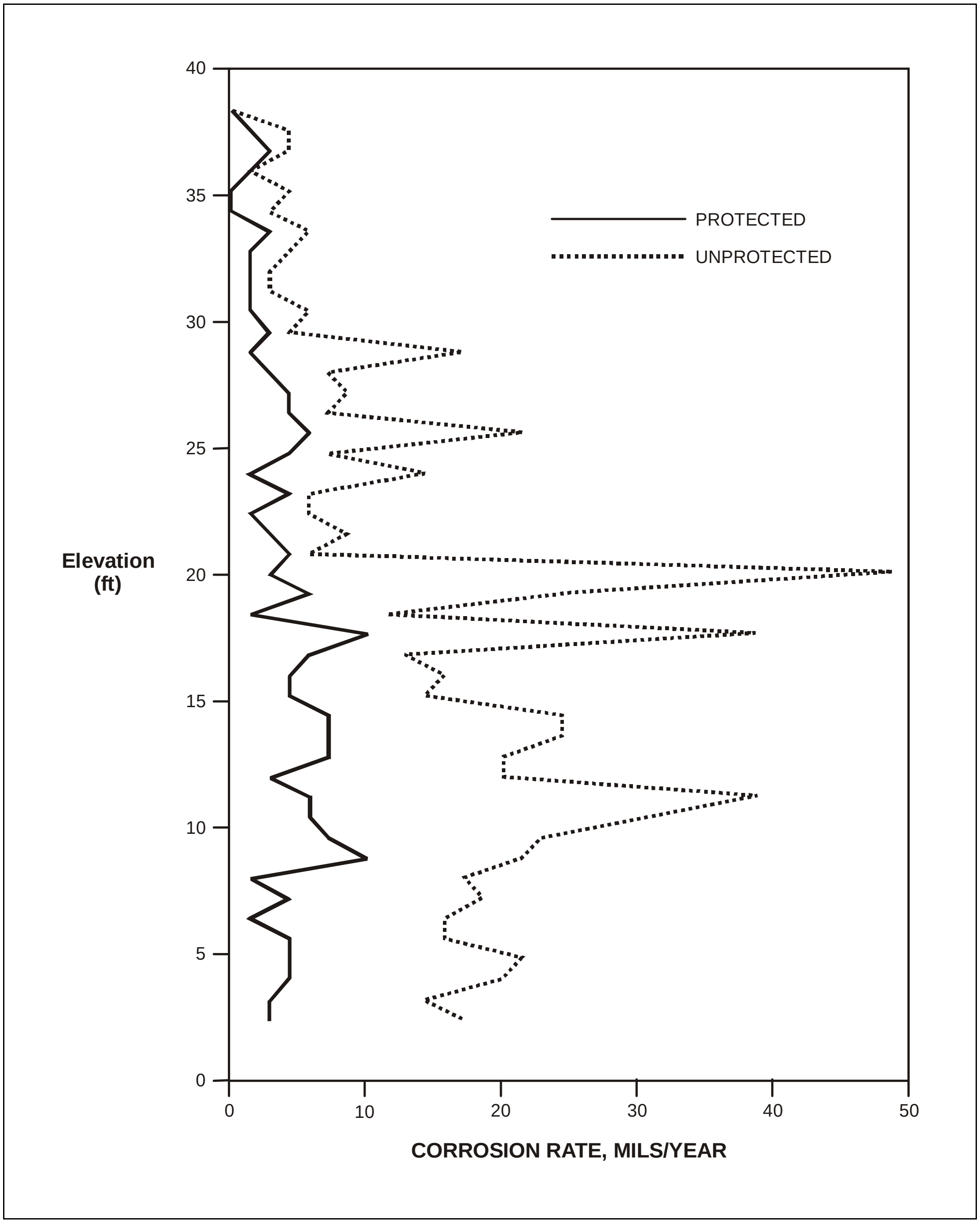


Fig. 11: *Corrosion rates at different elevations on protected and unprotected rods suspended in a green liquor storage tank.*

Bibliography

1. Paulonis, M. A. and G. A. Krishnagopalan, Kraft White and Green Liquor Composition Analysis. Part I: Discrete Sample Analyzer, Journal of Pulp and Paper Science, Vol. 20, No. 9, September, 1994.
2. Smook, G. A., Handbook for Pulp and Paper Technologists, Joint Textbook Committee of the Paper Industry, TAPPI and CPPA, 1986, p. 124.
3. O. Riggs, Jr., C. E. Locke, Anodic Protection, Theory and Practice in the Prevention of Corrosion, New York, NY, Plenum Press, 1981.
4. Wensley, D. A. and R. S. Charlton, Corrosion Studies in Kraft White Liquor: Potentiostatic Polarization of Mild Steel in Caustic Solutions Containing Sulfur Species, Corrosion/79, Paper #187, NACE, 1979.
5. Locke, C. E., Anodic Protection for Corrosion Control, TAPPI, Vol. 49, No. 1, January, 1966.
6. Yeske, R.A., E. Hill, and S. Mindt, Anodic Protection of a White Liquor Clarifier, 1986 Fifth International Symposium on Corrosion in the Pulp and Paper Industry, NACE, Vancouver, Canada, June, 1986.
7. Munro, J. I., Anodic Protection of White and Green Kraft Liquor Tankage, Part I: Electrochemistry of Kraft liquor, Materials Performance, February, 2002.
8. Munro, J. I., Anodic Protection of White and Green Kraft Liquor Tankage, Part II: Anodic Protection Design and System Operation, Materials Performance, March, 2002.