Anodic protection is a powerful technique used to mitigate corrosion of liquor tankage. The large currents required for protection of a typical vessel led to problems in the first generation of commercial systems. This paper describes the cause of the problems and the solutions developed for successful protection systems. Use of protective linings utilized in conjunction with anodic protection shows great promise.

Anodic protection was first successfully undertaken during December 19841. This initial system continues to operate uninterrupted, providing a large reduction in corrosion rates. The success of this system resulted in many commercial installations.

Unfortunately, unexpectedly high corrosion rates were reported at localized areas in several of the tanks even though the remainder of the surfaces corroded at rates less than 5 mpy as predicted from lab and field data for protected carbon steel coupons and tankage.

The purpose of this paper is to discuss the most likely causes of high localized corrosion rates, the techniques necessary to prevent such occurrences and work underway to reduce the installed cost for protection of carbon steel tanks with and without the use of organic coatings.

**ELECTROCHEMISTRY OF KRAFT LIQUORS**

The electrochemistry of kraft liquors is complex due to the multiple oxidation states of sulphur compounds (Tables 1 & 2), the number of possible Fe-S-H₂O reactions and the existence of active-passive behaviour. Crowe3 published a list of 31 possible Fe-S-H₂O reactions. Crowe and Peterman3,4 suggest that additional reactions have been reported.

The electrochemistry may be further complicated as some Fe-S compounds are semi-conductors5. Active passive behaviour requires a negative resistance portion of the anodic curve. Voltage controlled negative resistance

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**TABLE 1 • Summary of Sulphur Species Including Valences in Kraft Liquor**

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Valence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>SO₄²⁻</td>
<td>-6</td>
</tr>
<tr>
<td>Sulphite</td>
<td>SO₃²⁻</td>
<td>-4</td>
</tr>
<tr>
<td>Thiosulphate</td>
<td>S₂O₃²⁻</td>
<td>-2</td>
</tr>
<tr>
<td>Sulphur</td>
<td>S</td>
<td>0</td>
</tr>
<tr>
<td>Polysulphide</td>
<td>Sₓ (x=1)</td>
<td>-1</td>
</tr>
<tr>
<td>Polysulphide</td>
<td>Sₓ (x=2)</td>
<td>-2</td>
</tr>
<tr>
<td>Sulphide</td>
<td>S²⁻</td>
<td>-2</td>
</tr>
</tbody>
</table>

**EQUILIBRIUM OF SULPHUR SPECIES**

Na₂S + Na₂S₂O₃ ↔ Na₂SO₃ + Na₂S₂

S²⁻ + S₂O₃²⁻ ↔ SO₃²⁻ + S₂⁻

At 50 °C, K = 1.6 x 10⁻⁴

S₂⁻ = K (S₂O₃²⁻) (S²⁻) / SO₃²⁻

**TABLE 2 • Equilibrium of Sulphur Species in Kraft Liquor**

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Anodic protection is a powerful technique used to mitigate corrosion of liquor tankage. The large currents required for protection of a typical vessel led to problems in the first generation of commercial systems. This paper describes the cause of the problems and the solutions developed for successful protection systems. Use of protective linings utilized in conjunction with anodic protection shows great promise.

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devices are uncommon in disciplines other than electrochemistry. It is interesting to note that a semiconductor device called a tunnel diode exhibits near identical behaviour to active-passive interfaces. Additional work is required to determine if semiconductor films are significant to corrosion studies in kraft liquors.

Tromans\(^5\) deduced an elegant yet simple model of passivation in caustic sulphide which explains the role of sulphide in the process. He concluded that after the initial nucleation of Fe\(_3\)O\(_4\), sulphide is incorporated into the lattice creating a compound Fe\(_3\)O\(_4\)\(_x\)S\(_x\) which is nonprotective. At the peak of the active-passive transition, he predicted \(x\) to be approximately 0.19. Passivation does not occur until the sulphide in the film is removed by oxidation. In order for this reaction to proceed, high current densities are required. However, once devoid of sulphide, the film will remain stable if the potential is kept more positive than the Flade potential by the reduction reaction of oxidized sulphur species such as S\(_2\)O\(_3\) and S\(_2\)\(^2\)\(^-\).

Astable behaviour occurs infrequently as it requires a single anodic/cathodic intersection on the negative resistance portion of the anodic curve. This is an unstable operating condition resulting in continuous oscillations between active and passive potentials. Various alloys in elevated temperature sulphuric acid exhibit astable behaviour\(^6\).

These four types of mixed potential models are simplistic and do not accurately reflect the behaviour of carbon steel in liquors because the models assume that the reactions are time invariant.

Figure 6 depicts typical curves from an in situ test in a white liquor clarifier at different scan rates. The passive state does not exist until after the active-passive transition is traversed. Therefore, unless sufficient anodic current density is discharged from carbon steel by a naturally occurring cathodic reaction or an applied anodic protection current, the carbon steel/liquor interface remains monostable (active) as the passive film and its low current density properties do not exist.

Figure 1 depicts one anodic and four cathodic idealized polarization curves including the possible intersection points. The number and location of the intersection points creates four types of behaviour namely Monostable (active) Bistable, Astable and Monostable (passive). A potentiodynamic curve of each of these types of behaviour is shown in Figures 2 through 5.
As predicted by Tromans and verified by typical curves, once the active-passive barrier is traversed then bistable behaviour is possible. When the direction of the curve is reversed, a second stable equilibrium potential is established. Morris(6) used this knowledge to determine protection potentials for stainless steel and high nickel alloys in elevated temperature sulphuric acid.

Anodic Reactions Prior To Traverse of Active-Passive Boundary

Anodic protection and potentiostat induced passivity requires some finite period of time of operation in the active zone. Tests were performed by Thompson(7) to establish the corrosion rate during these periods. A carbon steel specimen was potential controlled at the peak of the active zone for 21 hours during which time the current was carefully monitored. The current density averaged 12.5 mA/cm². Assuming all of the current caused corrosion of iron to the Fe³⁺ oxidation state then the Faradaic loss would have approached 3800 mpy. The actual measured corrosion rate however was only 362 mpy. (The data are summarized in Table 3.)

Integration of 20 cycles of the anodic curve predicted a penetration of 0.17 mils for a single traverse of the active zone. However, the experimental results indicated a value of 0.0135 mils per cycle (Table 4). Hence, iron oxidation accounts for only approximately 6-10% of the discharged current. The remainder of the current therefore must be consumed by oxidation of sulphide in the Fe₃O₄⁻ₓSₓ film or directly from the solution. This will lead to large quantities of oxidized sulphur species (S₂O⁻₃ or S⁻₂) in the diffusion layer next to the passivated surface. Presence of these reducible ions at the metal-solution interface should significantly increase the cathodic reaction rate.

The bistable condition that occurs after passivation is therefore not permanently stable. The anodic and cathodic curves intersect due to the oxidation of the Fe₃O₄-xSₓ and enhanced levels of cathodic reactants. This lack of stability was verified by passivating a coupon in stagnant white liquor for 3 days after which time the current was shut off. The potential of the coupon remained in the passive zone for two days after which it reactivated. The cathodic and anodic reactions became unequal so as to create only a monostable (active) operation. Spontaneous bistable conditions do not exist for carbon steel in white liquor. Bistable conditions can only occur after passivation and will not remain if the natural occurring cathodic reaction rate is less than the rate of the anodic reaction. Therefore, this bistable condition is better termed “forced bistable”.

Cathodic Reactions

In order to control corrosion, an anodic protection system must create and maintain the passive condition under all possible liquor chemistries. Under
monostable (active) conditions, the system must provide the required current density to passivate the steel as well as provide the steady state current necessary to equal the difference in the cathodic and anodic reactions at the optimum potential. If “forced bistable” conditions occur, the system must simply prevent reactivation. The control dynamics for these two cases can be significantly different!

Research has concentrated on the anodic reactions with less emphasis on the cathodic curves. Most work assumes a single cathodic reaction of polysulphide to sulphide in even low concentration polysulphide liquors. Thiosulphate is a known corrosion accelerator\(^4, 8-17\); in white and green liquors even though direct reduction of this ion is difficult to verify. Peterman\(^4\) concluded that thiosulphate was directly reduced in the corrosion reaction. His data showed that the thiosulphate concentration significantly affected the corrosion potential and corrosion rate.

Figure 7 is a plot of all available\(^4, 15, 17\) potential versus electrochemical equivalent weight loss data. The conversion assumes that iron corrodes to a Fe\(^{3+}\) oxidation state. This data came from many different liquor chemistries and experimental techniques including potentiostatic control, chemical additions and open circuit conditions. It appears that the corrosion rate is much more sensitive to potential than other known variables. Therefore the corrosion rates in high content thiosulphate liquor may not be an anomaly due to different corrosion products, etc. Thiosulphate may somehow affect the cathodic reactions.

Wensley\(^8\) reported that liquors containing high levels of sulphide and thiosulphate passivated carbon steel coupled to stainless steel. Crowe\(^4\) claimed that although thiosulphate appeared to be an oxidant, it could not passivate carbon steel at any concentrations.

The effects of thiosulphate may be explained by calculations performed by Tromans\(^5\) from equations provided by Biernat and Robins:

\[
E_{S_2O_3^{-2}/S^{-2}} = 0.034 - 0.056 \text{pH} + 0.0093 \log ([S_2O_3^{-2}] /[S^{-2}]^2)
\]

The equilibrium potential \(E_{S_2O_3^{-2}/S^{-2}}\) is -921 mV vs a saturated calomel electrode (SCE) or -21 mV vs a silver sulphide electrode (SSE) assuming an activity of 10\(^4\) moles/liter for the thiosulphate and 0.423 for the sulphide. This potential shifts approximately 10 mV in the positive direction for each order of magnitude increase in the thiosulphate activity. Assuming a reasonable Tafel slope for this reaction then an intercept more positive than the critical potential for passivation of carbon steel is not possible. Hence increases in the concentration of thiosulfate can increase the corrosion rate but cannot passivate carbon steel. At passive potentials, thiosulphate may be oxidized and hence play no major part in the reduction reaction.

Estimation\(^18\) of the equilibrium potential of \((S^{-2}/S_2O_3^{-2})\) puts it at approximately +100 to +150 mV versus SSE. Polysulphide reduction, therefore, can provide sufficient current to passivate carbon steel if enough polysulphide is present in the solution.

**Separate Active & Passive Areas in Anodically Protected Tanks**

As a result of the high conductivity of white liquor, several “myths” surround the use of anodic protection, one of which is that active areas will be galvanically polarized passive if the majority of surface is passive. In the forced bistable scenario however both a passive and active intercept are possible. Each is stable and can co-exist simultaneously as shown in Figure 8.
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The simultaneous existence of separate active and passive areas results in low and marginally higher than open-circuit corrosion rates respectively. This type of operation is far from optimum. However, it is not the worst possible scenario. Figures 9 and 10 indicate the effective film resistance for a sample of 1 cm² as a function of potential. The resistance is calculated from the slope of the polarization curves. The resistance is low in the active zone, negative from the current peak to the Flade potential and increases to large values in the passive zone. The film resistance in the passive zone is time dependent as can be seen from the data at the two scan rates.

The potential measured by a reference electrode is the weighted average of all potentials of a structure. The weighting factor is the resistance (solution and film) from the location of the various surfaces to the reference. The situation is complicated by an error voltage called IR created by protection current flow through the electrolyte. As a result of the large differences in surface resistance between active and passive areas, an active area is detectable by a reference at any location in the structure.

If an active area develops, the potential controlled current source (potentiostat) outputs more current in response to the lower reference potential. Unfortunately, the IR at the reference location increases the measured potential. The IR masks the evidence of the active area and the source outputs insufficient current to passivate the zone. Without sufficient current density to be passivated, small active areas increase in size. This results in a larger current output from the power supply on the active site. Eventually an equilibrium is established between the size of the active area and the current output. Unfortunately this results in a location (usually an ellipse) operating at the peak anodic current density of carbon steel in liquor and hence results in very high corrosion rates.

This type of operation was verified in a protected tank. System operation in this mode was easily corrected once the possibility of co-existence of active and passive zones was verified. The potential of an active area is so dominant due to the low resistance to the reference that it can be easily detected. Passivation of an active area is simple to accomplish if detected and repassivated when it is small.

Current Distribution in Liquor

White liquor exhibits a resistivity of approximately 1Ω-cm(15) which is 30 times more conductive than seawater. This high conductivity, coupled with the previously discussed large resistance of the passive film, can result in a conclusion that the current distribution in liquors is uniform regardless of the location of the cathodes. Unfortunately, this assumption is incorrect and can lead to incomplete passivation of liquor tanks.

Primary current distribution is solely a function of the geometries of the anode and cathode. All surfaces are considered non-polarizable and hence solution conductivity and electrode kinetics are eliminated from the calculations. Figure 11 depicts the primary current distribution calculated for a line-plane geometry. As the line electrode approaches the plane electrode, the uniformity of current on the plane decreases in a non-linear manner.

Secondary and tertiary current distribution assumes electrode polarization. If the electrochemistry of carbon steel in kraft liquors resulted in only a single current peak at the active-passive transition followed by a low current zone then polarization of the tank surface would result in very uniform current distribution. Unfortunately in white liquor the sulphide breakaway current prevents significant secondary distribution. This is shown graphically.
in Figure 12. Sulphide oxidation consumes the excess current density and hence this current cannot be distributed to other locations. Anodic protection of liquor tanks, therefore, must be designed on the basis of primary and not secondary current distribution.

**Potential Measurements in Anodically Protected Tanks**

Extensive potential data has been collected from approximately 40 white and green liquor tanks. The following is a compilation of general observations and conclusions from this information.

Unprotected potentials of all tanks (except 2) were -125mV ± 10 mV versus silver sulphide electrode (SSE) regardless of liquor type (white and green). One of the anomalous tanks indicated potentials of -110 and -80 mV at opposite points on the shell circumference. The potential of the other tank, which was fabricated using large amounts of stainless steel, was in the passive zone (+75mV (SSE)).

The most frequent potential range of -125mV corresponds within the accuracy of a SSE to the minor peak at -770mV SHE reported by Tromans(5). He concluded that this was the potential at which S-2 ions incorporate into the lattice.

Potentials in the immersed liquid/air interface are normally 5-10mV more positive than at the bottom of the tanks. The distribution of potentials is linear with depth of liquor. No abrupt change occurs at the interface between the wet/dry and constant immersed zone.

If a passivation attempt is aborted, the potentials move 10-20mV more negative than the “static” values. This change has remained for as long as two months.

If the anodic protection system is turned off, the potentials decay in the negative direction in three discrete steps. The initial step is rapid, decaying to a value of approximately -75 mV (SSE). This potential remains for days and in one case lasted 3 weeks. The next step occurs over hours and is linear with time to a potential of approximately -125mV SSE. These decay times correspond to the effective film resistance vs potential. Unlike initial passivation, the time required to re-establish the set potential is relatively short (1/2 hour), suggesting that the passive film was still intact. Perhaps reincorporation of S-2 back into the film is not reversible or more likely is very time dependent.

When anodically protected tanks are cleaned of lime mud and FeS deposits, the underlying surface possesses a bronze coloured hue. This thin film is thought to be either FeS₂ (pyrite) or NaFeS₂ · 2H₂O.

**Summary of the Problems Encountered with Anodic Protection of Liquor Vessels**

Most of the problems experienced so far have resulted from incomplete understanding of the electrochemistry of carbon steel in liquors and the assumption that the current distribution was secondary and not primary. This caused the creation of active and passive co-existing areas. Fear of high corrosion rates during passivation rushed the passivation process which probably increased the number of active locations. Earlier control philosophy did not account for the possibility of active and passive co-existing sites. Present systems recognize and avoid these problems.

**ANODIC PROTECTION DESIGN & SYSTEM OPERATION**

**General:** Design of the protection and control systems now incorporates all of the features required to passivate the tank, maintain passivation, detect active areas and repassivate if required. The general system layout is shown as Figure 13.
**Cathode Design:** The location of cathodes affects the current distribution to the tank walls. Design is based on primary current distribution with the ratio of the minimum to maximum current density around the circumference of the tank greater than 0.9.

The design of the system must allow for a fluctuating liquor level. This requires higher initial current density and more frequent repassivation cycles to form a tenacious passive layer. When immersed, the wet/dry zone of a tank exhibits a more positive potential than the remainder of tank which may account for the higher corrosion rates there. However, it has been observed that the wet/dry zone does not get covered with surface build-up or deposits. The constantly immersed zone builds a thick surface deposit on these protected surfaces. All of the electrochemistry previously discussed is also applicable to decanted liquor. Surface build-up probably diffusion limits all of the reaction rates.

**Control System:** Conventional control schemes for electrochemical protection systems rely on a simple PI (Proportional, Integral) algorithm. This technique is not optimum when active and passive areas exist simultaneously. The use of this type of control resulted in accelerated corrosion of active areas.

When a surface is entirely passive, the measured potential is uniform to within a few millivolts around the circumference of the tank. An active area of any size significantly distorts this uniformity. The measurement is so precise that active areas can be located by triangulation.

Once this distortion is detected, the control system initiates an automatic repassivation using high currents for a programmable period of time. Once repassivation is completed, the system is retested to ensure uniform passivity.

Implementation of this scheme has revealed when and where active areas are formed on the vessel. Once the cathode design was modified to provide uniform distribution of current, all activations have occurred only at the wet/dry zone soon after initial passivation. The initial stability of the passive film in this zone is less than at other locations. Several repassivations are common during the first month of operation. Activations seldom occur after this stabilization period.

**Corrosion Rate Measurements of Protected Tanks**

After discovery of the possible problems affecting anodic protection of tanks and clarifiers, it was considered essential to verify that the implemented solutions resulted in significant reductions in the corrosion rate in both the wet/dry and immersed zones of tankage. Multi-wire coupons that extend from the top to the bottom of the tank are one way to do this. One of the wire coupons is protected via a direct connection to the tank while the second is isolated to simulate unprotected corrosion rates. A third stainless steel wire supports the other wires.

These coupons were originally 3.17 mm O.D. which proved to be sufficient cross sectional area to duplicate corrosion rates in unprotected tanks. The coupons appear to corrode at a slightly higher rate than the actual tankage in the immersed zones probably due to lime mud effects, however the wet/dry zone give results that correlated well with actual tank thickness loss.

As a result of the high current density required to initially passivate a vessel and attached coupons the 3.17 mm O.D. coupons proved to have too large a lineal resistance to ensure passivation. Coupons have since been increased in diameter to ensure they accurately model the tank. Typical corrosion rates for protected and unprotected coupons are shown in Figure 14.

In addition to coupon testing, several tank shells were thickness tested by carefully taken ultrasonic readings. One of the tanks had previously...
suffered from accelerated active corrosion. It is being tested internally using a 2' x 2' grid. The results indicate less than 6mpy average corrosion rate.

In a clarifier that is being monitored using both internal and external ultrasonic thickness measurements, the corrosion rate appears to be well under 10 mpy.

Monitoring of these vessels will continue and attempts are underway to measure thickness loss on tankage with more than 5 years of protected operation.

**Installed Cost Reductions of Systems**

The majority of costs associated with present anodic protection for liquor vessels is for the supply and installation of the heavy capacity cable needed to transmit high current, low voltage D.C. power from the tank to the controlled current source. Future systems are planned that will not require large size wiring, conduit nor cable tray. This second generation of system is expected to significantly reduce the installed cost of anodic protection systems for liquor vessels.

**Anodic Protection and Protective Linings**

The failure mechanisms of linings include direct chemical attack of the coating, corrosion undercutting at coating misouts or damage and blistering due to osmotic pressure. Loss of bond of inadequate coatings can result from alkalinization of the interface. Caustic resistant coatings are formulated to minimize this type of interfacial degradation. Proprietary low temperature baked epoxy linings have been utilized for white, green and heavy black liquor storage tanks and clarifiers. Most of these have been recently applied and limited inspection information is available.

**Protective Linings Utilized in Conjunction with Anodic Protection**

Organic linings are routinely utilized as the sole corrosion protection scheme for industrial tanks and transportation equipment. The linings have been specifically formulated for the service conditions. Sulphuric acid, 50% caustic and other chemicals used by the pulp and paper industry are usually shipped in railcars and tanker trucks lined with such material.

The application of protective linings is a specialized discipline and must be carried out under carefully controlled conditions. In liquor tanks it is essential that the surfaces be cleaned of caustic and sulphide contamination. Coating of deeply pitted surfaces puts more demands on the coating. Coatings and linings must be maintained to provide expected service.

![FIGURE 14: White Liquor Clarifier Corrosion Rates (mils/year)](image)
the other was isolated. Upon removal of the coupons, significant differences were visible. The anodically protected coupon showed no evidence of coating undercutting and the exposed carbon steel was covered with a thin black film under which was a grey passive layer. No measurable penetration was detectable. The unprotected coupon showed opposite results.

The second test involved potential measurements and current requirements testing in a green liquor storage tank lined with the same material used for the coupon test described above. A small amount of uncoated stainless steel was present in the tank. The potentials measured were between active and passive values for uncoated carbon steel. Interpretation of these measurements will require additional testing. The current density required to “passivate” the vessel was approximately 2% of the value required for uncoated carbon steel in green liquor. It is hoped that the mill can be convinced to install a small anodic protection system to protect any tank areas where the lining is, as well as to monitor the rate of coating degradation.

CONCLUSIONS

- Under normal operating chemistries in white and green kraft liquors, carbon steel exhibits a monostable (active) behaviour. Corrosion rates depend on presence of reducing agents (or cathodic reactions).
- Bistable behaviour occurs only after the passivation process has reached some degree of completion.
- Once created, the passive state is not spontaneously permanently stable.
- During traverse of the active zone, the corrosion rate is approximately 10% of the calculated Faradaic equivalent hence 90% of the current is consumed in sulphide oxidation.
- The role of thiosulphate in the corrosion process requires additional research.
- Active & passive areas can co-exist.
- Current distribution in anodic protection system design should be based on primary currents for high caustic and sulphide containing liquors.
- Operating tanks exhibit corrosion potentials values in the range of -125mV versus SSE regardless of liquor type.
- Corrosion potentials are approximately 10mV more positive in the upper zones of tanks.
- Anodic protection reduces the corrosion rates significantly once the system is designed to account for kraft liquor electrochemistry.
- Protective linings in conjunction with anodic protection may be a cost effective corrosion mitigation scheme.

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The authors of the referenced papers are gratefuly acknowledged. We wish to thank all of our fellow corrosionists for enduring the time required to solve the problems with anodic protection systems of liquor tanks. Special thanks goes to David Bennett, Pat Morris and Sandy Sharp for encouragement to continue the quest when it appeared hopeless. Review of Walter Mueller’s work reaffirmed his ability to question and solve the most important issues concerning electrochemistry in kraft liquors.

BIBLIOGRAPHY