

# Papritection® for the Bleach Plant of the 90's

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More than 100 Papritection® systems for bleach plant washers have been installed over the past decade. Long-term monitoring data from these systems shows that electrochemical protection can more than double the lifetime of a bleach washer, sufficient to pay back the capital and operating costs in a year.

Papritection®, an electrochemical corrosion protection system for bleach plant washers, was developed in the mid-1970's in response to the increasingly corrosive bleach plant filtrates being found in Canadian kraft mills<sup>[1,2]</sup>. New energy conservation and pollution control measures meant that the industry standard 317L stainless steel could not longer adequately resist corrosion in the strongly oxidizing washer filtrates. Papritection® provided a cost-effective alternative to purchasing new washers made from much more expensive alloys. The first commercial Papritection® system was energized in 1978, and to date, over 100 systems have been installed in kraft mills around the world.

More than a decade later, bleach plant operating practices are once again expected to change due to the implementation of even more stringent pol-

lution control measures<sup>[3]</sup>. In particular, high levels of chlorine dioxide (ClO<sub>2</sub>) substitution in the C-stage raise the spectre of more corrosive bleach plant filtrates. This makes it an opportune time to review how well Papritection® systems have performed to date, and to predict how they might perform under these new bleaching conditions. Will Papritection® remain a reliable option for protecting bleach plant washers in the 1990's?

## WHAT IS ELECTROCHEMICAL PROTECTION?

When residual chlorine (Cl<sub>2</sub>) or ClO<sub>2</sub> in the filtrate contacts the surface of a washer drum, reduction to chloride (Cl<sup>-</sup>) can occur via one of the following reactions:

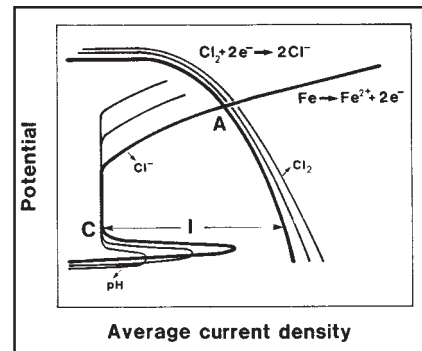
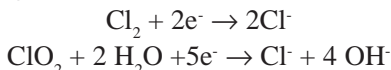


FIGURE 1 • Schematic polarization curves for reactions occurring at the surface of a stainless steel washer.

Corrosion of metal provides the source of electrons, for example, by the anodic dissolution of iron via:



Electrochemical protection works by using electricity to reduce the Cl<sub>2</sub> or ClO<sub>2</sub> on the surface of the drum. Schematic polarization curves can be used to illustrate how the cathodic and anodic reactions occur on the washer surface (Figure 1). Due to the presence of residual oxidant in the filtrate, the

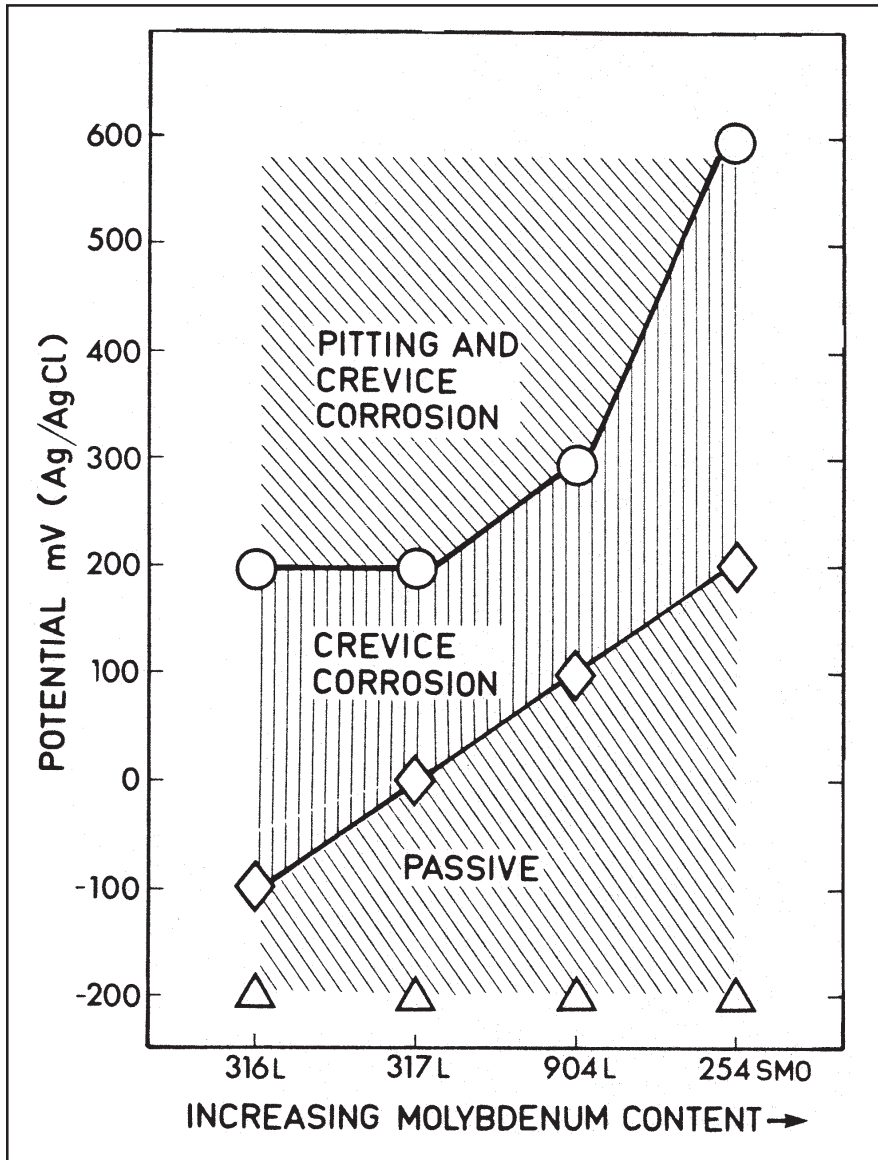


FIGURE 2 • Potential ranges for pitting and crevice corrosion, crevice corrosion alone, and passivity, for four austenitic stainless steels in synthetic C-stage washer filtrate.

equilibrium potential of the washer is found at Point A, where the anodic and cathodic curves intersect. The corrosion current density is very high under these conditions, and stainless steels undergo both pitting and crevice corrosion.

If the washer potential is lowered to Point C, where stainless steel is passive, the corrosion current is minimized. This can be done by passing a current, equal to the protection current I, between an inert anode and the

washer. While it is possible to make the washer potential even more negative than Point C, this is not done because of the presence of a region where active corrosion occurs. The effects of increasing pH, Cl<sup>-</sup> concentration and oxidant concentration (Cl<sub>2</sub> or ClO<sub>2</sub>) on the corrosion current are also shown on the diagram.

The optimum potential to protect bleach plant washers was determined by means of constant-potential laboratory tests covering a range of filtrate

compositions and potentials. Typical results are shown in Figure 2. Note that corrosion potentials in washer filtrates usually vary between +100 and +400 mV<sub>Ag/AgCl</sub>, depending on the residual oxidant concentration present. Although the higher alloys like 904L and 254 SMO are clearly more resistant to corrosion than 316L and 317L, even they cannot resist corrosion in all washer filtrates.

In a bleach plant washer, the protection potential is obtained by using a potential-controlled rectifier to pass a current between the washer drum and one or more inert anodes inserted along the length of the vat (Figure 3). A reference electrode is installed in the vat to measure the corrosion potential of the washer, and provide a signal for control of the rectifier. Additional hardware (for safety interlocks, etc.) is required to make up a complete Papritection® system (Figure 4).

In most cases, the effectiveness of protection is assessed by means of monitor coupons mounted on the end of the rotating washer drum. Two coupons are mounted so that each is in contact with 20 crevicing sites formed by segmented disk washers<sup>[4]</sup>. The mounting details are identical for the two coupons, except that one is kept in electrical contact with the drum, while the other is electrically isolated, so as to provide a comparison between protected and unprotected exposure. At

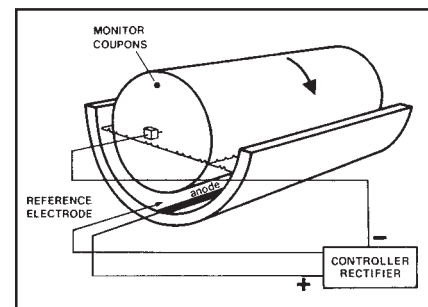


FIGURE 3 • Schematic of an electrochemical protection system for bleach plant washers.

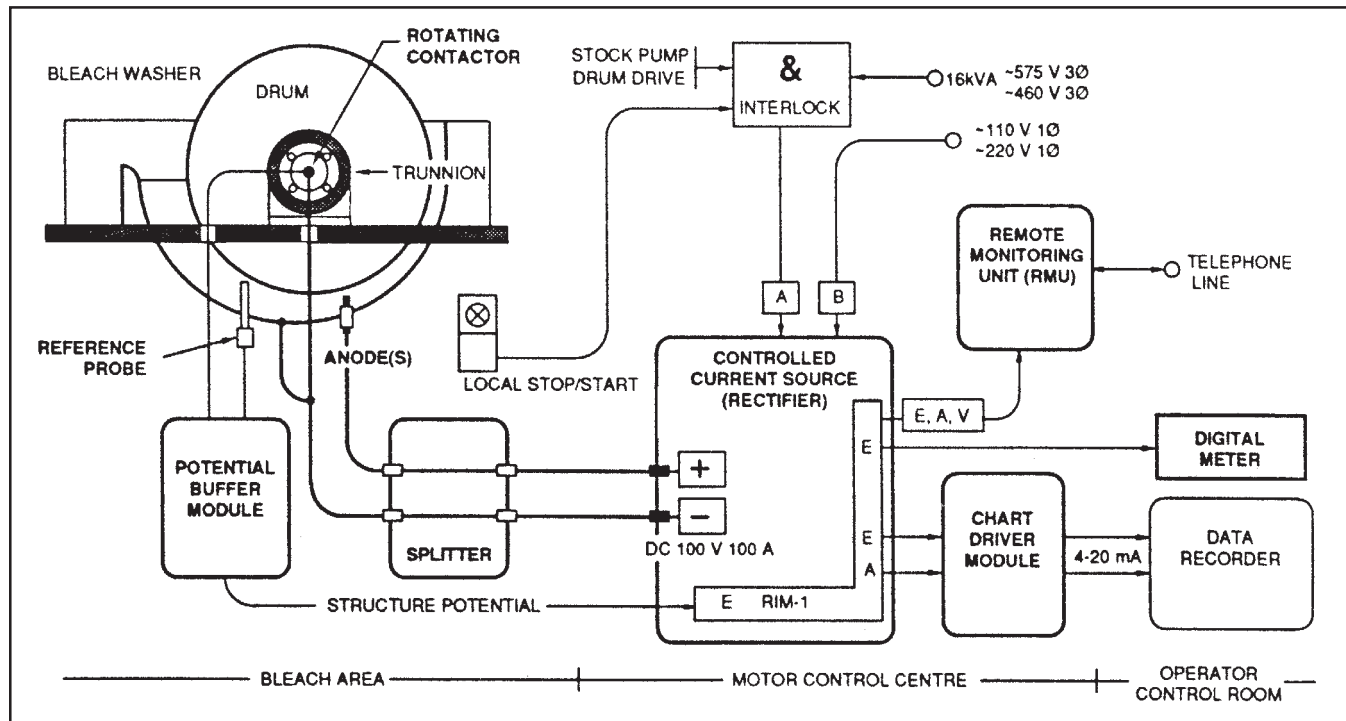


FIGURE 4 • Block diagram for a typical Papritection® system.

the end of a 60 day period, the coupons are removed and assessed for damage (Figure 5). Since coupon weight loss has been found to be as reliable an indication of the comparative severity of crevice or pitting corrosion as measurements of the depth of attack, it is used routinely to assess the effectiveness of protection.

In newer systems, the coupon monitoring is supplemented by the provision of a remote monitoring unit (RMU). The RMU monitors washer potential, rectifier output voltage and current, and whether or not the system is energized. This information is collected and stored for up to eight days. The RMU is interrogated weekly by the system vendor (or more frequently, if requested) to ensure that operating parameters are within preset limits. The mill is immediately informed if the data is outside the limits; otherwise a monthly report is issued.

A common misconception about electrochemical protection systems is that

they can prevent corrosion of the entire washer drum, including the carbon steel internal components. Electrochemical protection works primarily on a line-of-sight basis, and the throwing power is limited, depending on the conductivity and residual oxidant concentration of the filtrate. Thus, the largest effect is on the surface of the drum, where the clothing material forms tight crevices with the deck of the washer. Due to the formation of

these crevices, this area of the washer drum is the most susceptible to corrosion. Protection of the drainage tubes leading to the grapefruit valve is usually not possible, although the grapefruit valve itself can be protected by a separate electrochemical protection system.

### HOW EFFECTIVE IS PAPRITECTION®?

Since the installation of the first commercial system, data on the performance of Papritection® systems has been continuously accumulated by means of a comparative coupon monitoring program. Results from this program are shown in Figure 6 for pairs of coupons returned to the Pulp and Paper Research Institute of Canada for assessment. Most Papritection® systems have been installed on 317L washers, although 904L washers have also been frequent targets of electrochemical protection. A much smaller number of washers made from either

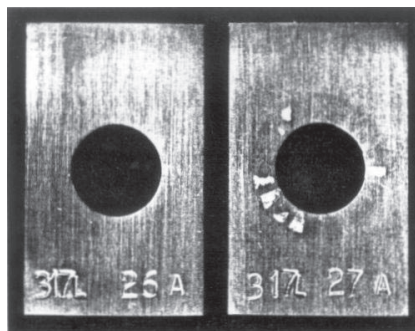


FIGURE 5 • 317L stainless steel monitor coupons after a 60-day exposure attached to a C-stage washer. The coupon on the left was protected, while the coupon on the right was unprotected and sustained crevice corrosion on 7 of 20 possible sites.

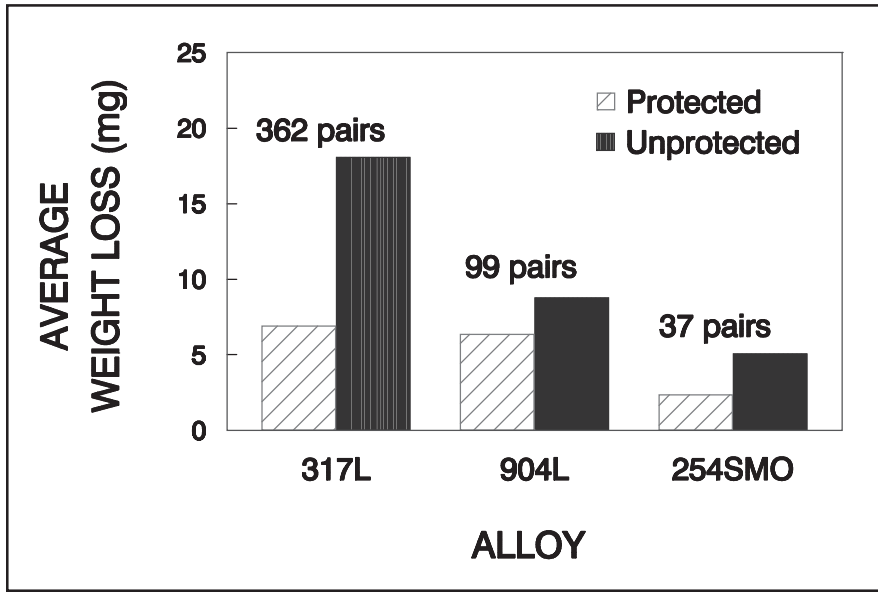


FIGURE 6 • Average weight loss for protected and unprotected coupon pairs over the lifetime of the monitoring program for 317L, 904L, and 254 SMO-type stainless steels.

254 SMO or 1925 hMo (both are premium alloys containing at least 6% molybdenum). Due to the limited number of either 254 SMO or 1925 hMo coupons returned, they have been grouped together under the 254 SMO banner. The number of pairs of coupons used to calculate the average coupon weight loss is indicated for each alloy type. As expected, the average unprotected weight loss of 317L

is much higher than for 904L or the 6% molybdenum containing alloys. 904L was twice as resistant to corrosion as 317L, while 254 SMO-type alloys were 3.6 times more resistant.

The protection ratio (the corrosion rate of the unprotected coupons divided by the corrosion rate of the protected coupons) for 317L is 2.7, while for 904L and 254 SMO, the protection ratios

were 1.4 and 2.0, respectively. Note that high values of the protection ratio indicate better performance of the Papritection® system. The exposure times for these coupons varied from a low of about 30 days to as long as one year.

The same data has been broken down by washer stage (C- or D-stage) and divided into categories which show the percentage of protected or unprotected coupons which had good (< 1 mg/cm<sup>2</sup>/y), medium (1 to 2 mg/cm<sup>2</sup>/y) or poor (> 2 mg/cm<sup>2</sup>/y) corrosion rates (Figures 7 & 8). The beneficial effect of Papritection® is particularly apparent for 317L coupons exposed in C-stage washers. By far the majority of the protected coupons fit into the good category, while unprotected coupons were much more likely to have corroded sufficiently to fall into the poor category. The data for the 904L coupons is similar, although the coupon results are more evenly divided between categories. Almost all of the 254 SMO type coupons returned fell into the good category, as would be expected for this class of alloys. However, a surprising percentage of unprotected coupons of this alloy type did

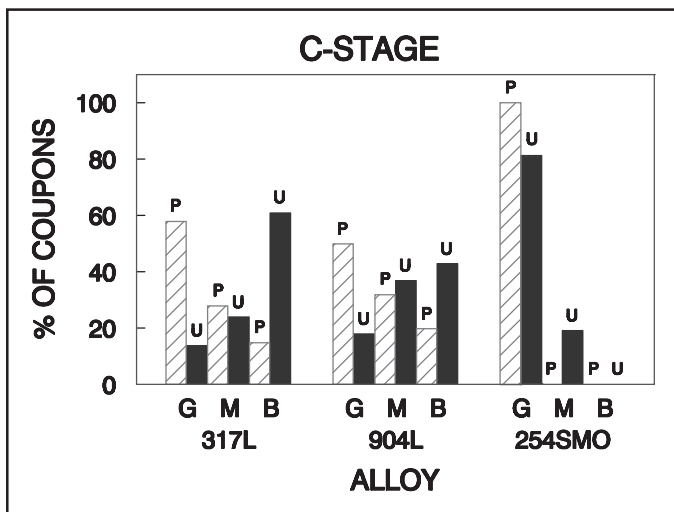


FIGURE 7 • The coupon data from Figure 6 for C-stage washers.

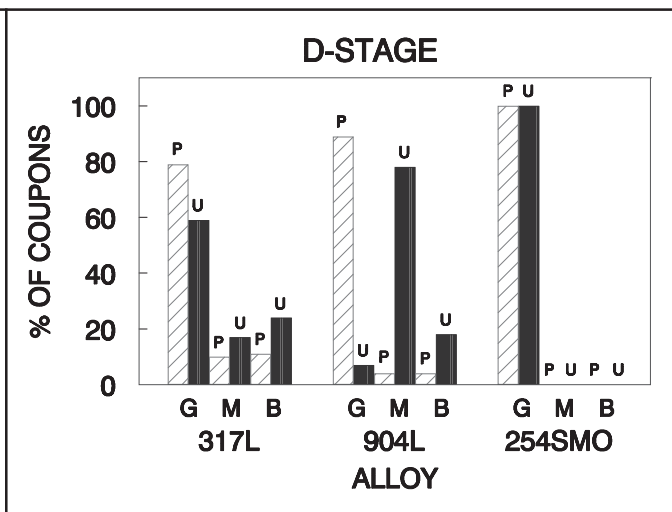
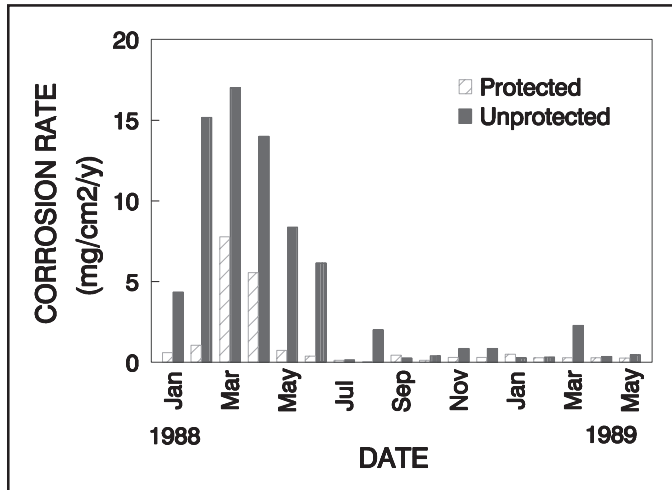
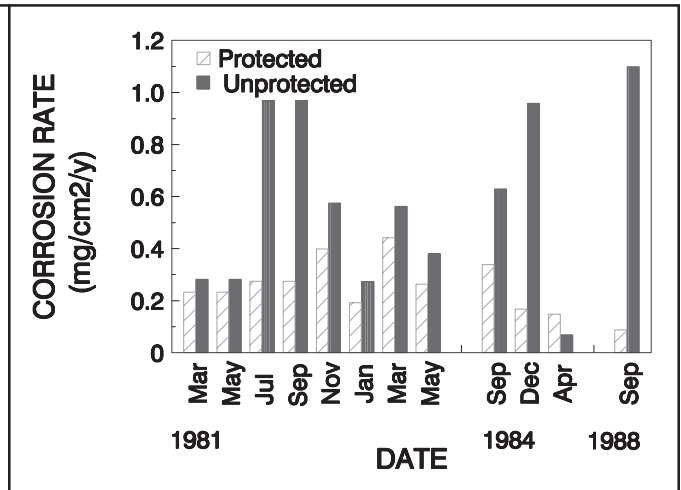


FIGURE 8 • Coupon data from Figure 6 for D-stage washers.

The data for both figures has been divided into the percentage of coupons (protected or unprotected) which fall into good, medium, and bad corrosion rate categories for each of the three stainless steels.



**FIGURE 9** • Results from monitoring coupons returned from a protected C-stage washer over a period of 18 months. The high corrosion rates which occurred in the first part of the monitoring period are typical of upset operating conditions.



**FIGURE 10** • Similar data to Figure 9 for a D-stage washer. These coupons were exposed for approximately 60 days. Gaps in the data represent periods when coupons were not returned for evaluation.

suffer significant corrosion. Far fewer coupons corroded sufficiently to fall into the medium or poor categories in D-stage washers, compared to the C-stage washer results.

Note that the above data is essentially unfiltered; that is, it contains results from a significant number of coupons which were exposed during periods of partial operation, or which were thought to be incorrectly installed. In particular, the relatively poor protection ratio for 904L can be attributed to one mill in which many coupons received only partial protection. This particular system was the first installed in a washer with a bare metal vat, and as discussed later in the paper, many problems were encountered in maintaining adequate protection of the washer. Consequently, the above data represent the worst-case long term benefits of Papritection®.

Results from closely monitored and well maintained Papritection® systems are substantially better than the average results shown above. Figure 9 gives monthly exposure data from one C-stage washer for a period of over 18 months, beginning in June, 1988. The

protection ratio for this washer (the corrosion rate of the unprotected coupon divided by the corrosion rate of the protected coupon) varied over this time period from a high of 34 to a low of 0.6. The average protection ratio was 5.5. Similar protection ratios have been reported for other C-stage washers and different time periods<sup>[5]</sup>. These results also show that low protection ratios are most often associated with periods of relatively non-corrosive operating conditions. Conversely, high protection ratios are found when conditions in the washer are extremely corrosive. High protection ratios have been correlated to periods of sustained operation with high residual oxidant<sup>[5]</sup>.

Similar data is available for D-stage washers (Figure 10). Over a four year operating period, the protection ratio for this washer varied from a high of 5.7 to a low of 0.4. The average protection ratio was 1.9. Note however, that corrosion rates for this washer were substantially lower than for the C-stage washer, low protection ratios are most often associated with low corrosion rates, while higher protection ratios result from significant increases in

corrosion rate of the unprotected coupon. Coupons in this washer were exposed for periods ranging from 61 to 137 days, rather than the 30 day exposures of the C-stage coupons reported above. Longer exposure periods tend to average out the effects of short term operation with high residual oxidant, which leads to rapid corrosion of the washer drum. This data is also consistent with previously published data of Papritection® performance<sup>[5]</sup>.

### WHAT PROBLEMS HAVE BEEN ENCOUNTERED?

One of the most frequent causes of poor performance of electrochemical protection systems like Papritection® is failure to keep the system energized. Automatic interlocks are provided with the stock pump and the drum drive, and when either of these are turned off, the system is disabled to prevent accidental contact with the anode when using a metal lance to clear dewatered pulp from the vat. A manual disable switch is also provided adjacent to the washer for cleaning on the run. Often, the system is not turned back on after such an outage (for ex-

ample, a review of operating data from one mill showed that the system was not energized 37% of the time as a result of manual shutdowns). Continuous operation is important because it is the short-term intermittent process upsets which cause the washer to corrode, rather than steady state operation.

The most effective way to solve this problem is to provide a means of automatic, continuous monitoring of the system operation to the vendor. A remote monitoring unit or RMU monitors the operating parameters of the Papritection® system, and is interrogated regularly by the vendor. The RMU also acts as an early warning device for impending failure of components like the anode. Monitoring coupons will also indicate when the system is not operational, but the feedback is much slower due to the time delay between coupon installation and coupon evaluation. It has been our experience, however, that mills which take the trouble to routinely return coupons catch problems quickly, and generally have much better operating protection systems as a consequence.

Some early systems suffered from having installed too small a rectifier to handle extreme upset conditions with high residual oxidant levels and low pH filtrate. This problem has essentially disappeared as these mills have upgraded to the now-standard more powerful rectifiers.

Premature anode failure has also occurred in some systems. This has been attributed to a combination of interactions between the anode and chlorinated organic material in the washer, and the type of waveform delivered by the rectifier. Solutions in this case have been to increase the thickness of the platinum layer on the anode, reduce the current density by adding more anodes to the system, and to signifi-

cantly reduce the AC ripple on the rectifier output current. Alternate anode materials are also being investigated, but none has yet been found to offer all of the advantages of the currently used anodes.

Protection of washer drums installed in bare metal vat washers has one of the most difficult and expensive situations in which to provide electrochemical protection<sup>[6]</sup>. Depending on anode placement, the metal vat can distort current distribution to the drum, and give non-uniform protection. The optimum location for the anode in this situation is equi-distant between the drum and the vat, but this is not practical since the anode would then be susceptible to damage when lancing the vat.

Increasing the number of anodes from one to three improves the current distribution, but not sufficiently to deal with high residual oxidant levels. The current approach is to use three anodes and install non-metallic pads under each of the anodes to shield them from the vat. Applying a non-metallic coating to the entire wetted surface of the vat solves the current distribution problem entirely, but must be balanced against the cost of periodic maintenance of the coating.

### HOW WILL PAPRITECTION® WORK IN FUTURE BLEACH PLANTS?

The most significant change to current operating practice in the bleach plant will be the use of higher ClO<sub>2</sub> substitution levels. Filtrate temperatures may also increase, due to a higher degree of closure in the mill<sup>[1]</sup>. Although higher filtrate temperatures are more corrosive, in that they make the alloys less tolerant of residual oxidant in the filtrate, this effect may be tempered by the fact that Cl<sub>2</sub> and ClO<sub>2</sub> will react

more quickly and therefore there will be less oxidant present to cause corrosion.

As far back as 1985, most Canadian mills reported some degree of substitution<sup>[7]</sup>, and it is expected that the degree of substitution by ClO<sub>2</sub> will increase up to and beyond the 50% level over the next few years<sup>[8]</sup>. The optimum operating pH for the new bleaching conditions has not yet been established, but it is expected that the pH in C or C/D stages will be relatively unchanged for up to 50% ClO<sub>2</sub> usage, and may be slightly less acid for mills which move to 100% ClO<sub>2</sub> substitution. It is well known that addition of ClO<sub>2</sub> to C-stage washers significantly increases corrosion<sup>[9]</sup>, but experience to date suggests that this effect is not sensitive to the actual level of ClO<sub>2</sub> substitution<sup>[7]</sup>.

Other innovations in the kraft mill, like oxygen delignification, improved brown stock washing, and improved medium and high density mixing should reduce the demand for oxidant, and thus reduce the overall level of residual oxidant reaching the washer. As a consequence, washer filtrates might be less corrosive than present.

Overall, it appears that the new bleaching conditions may not be significantly more corrosive than those which exist today. However, it is clear from alloy test rack exposures<sup>[10,11]</sup>, coupon monitoring data, and general experience, that today's washer filtrates are already so corrosive that 317L can no longer be relied upon to resist corrosion.

In 1985, a survey of C-stage washer corrosion found that over 30% of existing washers were made from 317L<sup>[7]</sup>. Without the addition of electrochemical protection, these washers will soon require replacement. A further 14% of the washers were made

from premium alloys like 254 SMO. While the coupon data indicates that these washers corrode much less than 317L or 904L washers, electrochemical protection still served to reduce the overall corrosion rates by a factor of two. Non-corroding washer materials like titanium and FRP accounted for only 24% of installed washers.

Cost studies have shown that if an electrochemical protection system can double the lifetime of a washer, the payback period for the capital and operating costs is about one year<sup>[5]</sup>. Even using the worst-case protection

data presented here, this performance can be achieved by electrochemical protection systems. Additional benefits, like reduced need for anti-chlor additions of SO<sub>2</sub> or NaOH make electrochemical protection even more attractive. Some mills have found an unexpected benefit to the installation of electrochemical protection to be that the current output is proportional to residual oxidant concentration. Thus, in addition to protecting the washer drum from corrosion, the output of the electrochemical protection system can be used to control the residual oxidant concentration in the vat.

### CONCLUSIONS

- More than a decade after the first commercial installation, electrochemical protection remains a viable option for the reduction of corrosion in bleach plant washers. With few exceptions, it has served to significantly extend the lifetime of washers which otherwise would have needed replacement. The basic system design has also improved and matured to reflect the experience gained from the coupon results, and from operation of the large number of installed systems.
- Although electrochemical protection was developed to extend the service life of 317L washers, the data presented in this paper shows that the benefits to premium alloys like 254 SMO are also substantial. A 254 SMO washer equipped with a Papritection® system still represents a state-of-the-art alternative to titanium or FRP washers.
- Overall, the long-term monitoring data presented in this paper shows that electrochemical protection consistently reduces corrosion by more than half, sufficient to pay back the capital and operating costs in a year. Well maintained and operated protection systems perform substantially better and show that electrochemical protection will remain a cost-effective means of reducing corrosion in the bleach plant of the 90's.

### ACKNOWLEDGEMENTS

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