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MATERIALS FOR PULPING AND PAPERMAKING APPLICATIONS

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ABSTRACT

Materials problems in the pulp and the paper industry are often traced to corrosion by aggressive environments that range from acidified oxidants to molten salts. Corrosion problems in the industry are likely to accelerate as a result of increased mill closure and water recycling. Higher corrosivity, together with escalating costs of labor-intensive maintenance, will lead to increasing reliance on highly alloyed materials for corrosion protection. Existing alloys can be identified which perform adequately in most pulp and paper process chemistries, but the industry would welcome lower cost materials with equal corrosion resistance. Expensive alloys will experience increasing competition from alternative corrosion control measures, particularly the increased use of nonmetals and anodic/cathodic protection.

INTRODUCTION

Although the materials used in the pulp and paper industry experience

wear, fatigue and other common forms of damage, the special afflictions of this industry are corrosion and corrosionassisted cracking. The corrosiveness of processes in the pulp and paper industry requires the use of exotic materials of construction with a correspondingly heavy capital costs burden. Operating costs associated with maintenance and loss of production are also high. Ten years ago, Davy and Meuller¹ fixed the annual cost of corrosion in the North American pulp and paper industry at \$300 million, which was roughly \$5/ton of fiber related product, exclusive of costs associated with loss of production. А large, 2000 ton/day mill operating 300 days per year can expect corrosionrelated costs totaling \$3 million/year, not counting lost production or the human costs of catastrophic, corrosion induced failures. Others have estimated the costs of corrosion in the industry to be somewhat higher. It is clear that corrosion-related damage is a significant concern for the pulp and paper industry.

The staggering cost of corrosion to the industry is clearly a consequence of the variety and overall aggressiveness of the liquors, waters, and other process streams involved in pulping, bleaching, papermaking, and chemical recovery. Few industries can match the number of different corrosive environments encountered in a single mill location. In a bleached kraft paper mill, for example, materials must withstand:

- alkaline sulfide cooking liquors at elevated temperatures and pressures
- chlorine gas used in bleaching applications
- highly oxidizing, acidified, chloride-laden bleachants
- paper machine white water, a nearly perfect growth medium for corrosion promoting organisms
- sulfurous acid conditions in electrostatic precipitators
- molten carbonate/sulfate salts in chemical recovery boilers
- slurries of lime mud and other abrasive compounds

Virtually every form of corrosionrelated damage to materials is encountered in a typical pulp mill on a discouragingly regular basis.

There have been several recent "epidemics" of corrosion-damage experienced by the pulp and paper industry. For example, following rupture of a large continuous digester used in pulping, stress corrosion cracking was discovered in roughly half of these pressure vessels in operation worldwide.² The costs in terms of repairs and lost production caused by this form of cracking have been enormous. Similarly, there have been numerous failures of suction press rolls and other perforated rolls involved in water removal on paper machines (Figure 1). $Garner^3$ has documented more than 190 failures of these rolls since 1960 in Canada alone. Uncertainty over lifetimes of these rolls and long leadtimes for replacement rolls have forced most mills to stock replacement rolls — a significant burden when rolls cost

several hundred thousand dollars and several rolls are involved. More recently, several catastrophic failures of storage tanks containing deaerated boiler feed water have prompted inspections that found more than half such vessels cracked in welds. It is sobering to reflect that these incidents are superimposed on a daily diet of less spectacular failures — thinning of pipes and tank walls, erosion-corrosion of pumps, valves and casings, corrosion of structural steel members, etc.

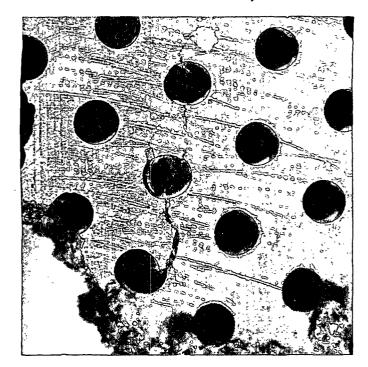


FIGURE 1--Section removed from a failed CF8M suction press roll

Although materials failures in the industry are distressing, and new modes of failure are being discovered daily, it is safe to say that most failures could have been prevented by selection of a more resistant material. With few exceptions, materials have been identified which are fully resistant to each of the aggressive environments encountered in the typical pulp and paper mill. Stainless steels are resistant to attack by alkaline sulfide pulping liquors, and titanium appears to be fully resistant to the very aggressive environments encountered in bleach plant washers. Acid-resistant brick and tile linings are effective over the long term in bleaching towers, and composite (carbon steel and stainless

steel) boiler tubes are resistant to fireside corrosion in chemical recovery boilers. A fully resistant suction roll alloy has yet to be demonstrated, but even here recent developments in cast duplex materials appear promising.

The problem with utilization of fully resistant materials of construction is, of course, cost. The price of materials with full corrosion resistance is often difficult to justify, particularly when the capital costs of a mill approach \$1 million per ton of production, as in a recent green field construction. To remain competitive, most mills adopt a strategy of repair and replacement of process equipment constructed from materials with less than optimal resistance to corrosion by a given process environment. When viewed in this light, corrosion damage in the paper industry is not caused by inadequacy of the present generation of materials, but rather by the high cost of optimal materials in relationship to the cost of periodic repair or replacement with less resistant (and less expensive) materials.

MATERIALS PERFORMANCE IN THE INDUSTRY

It is instructive to review the current materials of contruction in the pulp and paper industry to identify where the current generation of materials is inadequate and where improved, low cost alternatives are sought. Such a review must be eclectic, because the number of different process conditions and materials of construction is striking, and all cannot be covered. Indeed, there is no such thing as a "typical" mill, for each mill approaches pulping and papermaking in a slightly different way, based on its experiences and production objectives. Thus, each mill will modify process chemistries and select materials of construction in different ways, and the corrosion concerns that arise are variations on a theme of the generic corrosion experienced by the industry as a whole.

In spite of the idiosyncrasies of individual mills, it is possible to describe the process elements of the industry — pulping, bleaching, papermaking and recovery. Supplementary information is available in the corrosion literature⁴⁻⁸.

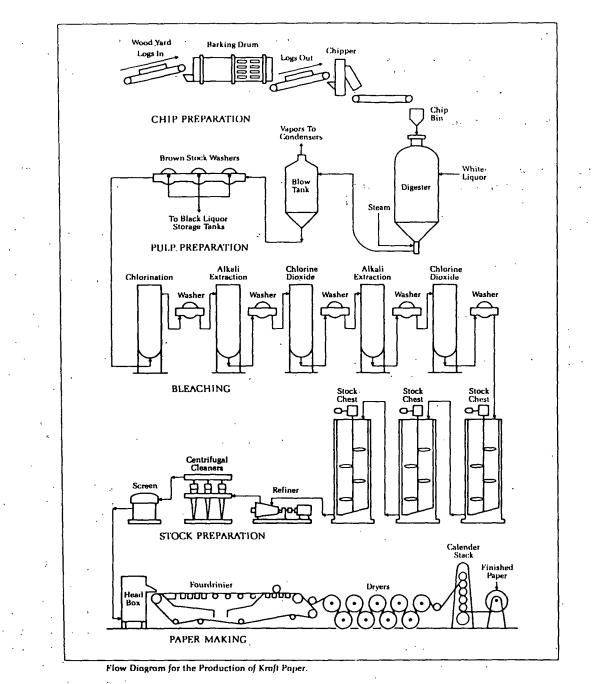
Pulping

Pulping Processes. Pulping involves the conversion of fiber raw materials, usually wood chips, to a form that is suitable for papermaking. Chemical pulping involves removal of the lignin binding cellulose fibers by chemical means, usually by exposure to hot alkaline sulfide or acidic sulfite cooling liquors. A schematic of the kraft pulping process involving continuous alkaline sulfide digestion of chips is shown in Figure 2. Mechanical pulping involves abrasion of wood to separate individual fibers, with retention of most of the constituents of wood in the pulp slurry. There are many combinations of chemical and mechanical pulping in practice today, as well.

Mechanical pulping processes are relatively free of corrosion concerns, so discussion is focused on the two principal chemical pulping processes, kraft and sulfite pulping. In a typical kraft process, wood chips are cooked in a liquor containing 10% NaOH and 2-3% Na₂S, at temperatures of 175° C (350° F). The cooking may be done continuously, as shown in Figure 3, or on a batch basis. In a typical sulfite process, chips are cooked in a neutral or acid sulfite solution whose pH may be as low as 1-2.

At the completion of cooking, the pulp mass is discharged to a holding vessel, followed by washing to remove the spent liquors from the cellulose. In continuous digesters, some washing is accomplished in the digester vessel, but rotary drum washers are also commonly used.

Corrosion Concerns in Pulping. In the kraft pulping process, the most common material of construction is carbon steel, such as A285-C or 516-Gr70 steels. Digesters may be lined with stainless steel, either by weld overlays or by use of stainless cladding. In





many mills, stainless steel vessels and piping are used to contain the kraft white liquors used to prepare cooking liquors. Some polymeric materials are used in the pulp mill, in applications such as fume hoods and duct work, but the high temperatures used in pulping restrict the widespread use of polymeric materials of construction.

Carbon steel is subject to uniform attack by kraft liquors, with corrosion rates of 20 mils/year being typical. Carbon steel surfaces exposed to high liquor velocity or heat transfer may experience much higher corrosion rates, so most batch digesters are overlayed with stainless steel, and there is a trend toward use of stainless steel piping in the kraft mill. Tanks and clarifiers fabricated from carbon steel have lifetimes ranging from five to twenty years before maintenance becomes troublesome and replacement is necessary. Kraft pulp washers are also made from carbon steel construction, and the combination of high pH (10-11) and inhibition by organic compounds in the spent liquors prevents serious corrosion.

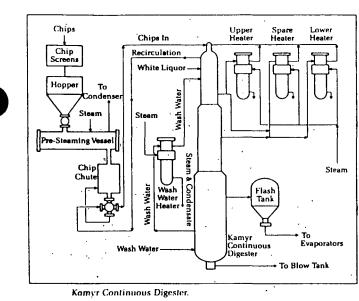


FIGURE 3--Schematic representation of the kraft pulping process using a continuous digester

Stainless steels are generally resistant to the conditions found in kraft pulping. Some degradation of stainless weld overlay in batch digesters is typical, as is stress corrosion cracking of stainless steel tubes in heat exchangers used to heat recirculating kraft cooking liquors. Both of these forms of damage are attributed to caustic cracking in the presence of concentrated caustic produced by heat transfer. Frequent acid cleaning to remove scales can also lead to high rates of attack on stainless steel surfaces if care is not taken in temperature control and chemical inhibition. Some duplex stainless steels appear to be fully resistant to this form of attack. Blow plates, against which pulp ejected from the digester impinges, are also subject to severe erosion/corrosion. Many mills are resigned to repeated replacement of these target plates, but duplex 26Cr-5Ni-3Mo alloys have shown good resistance in this application.

Fiber-reinforced polymerics (FRP) do not enjoy extensive use in the kraft mill because of the high temperatures involved. However, fume hoods over pulp washers and associated ductwork for odor-control systems are often fabricated from FRP.

Because of the acidic nature of sulfite pulping liquors; carbon steels are not suitable for digesters, piping, tanks or pulp washers in this process. In fact, type 304 stainless steel is usually marginal in most applications, and molybdenum-bearing 316L or 317L. stainless steels are preferred for use in the sulfite mill. For acid storage, tanks, accumulators, absorption towers, SO₂ cooling towers, and digesters, even the high molybdenum stainless steels may be inadequate, so acid resistant tiles and brick linings are commonly used. Where temperatures are moderate, fiber-reinforced polyesters are used in place of stainless steel.

Bleaching ...

The most challenging environments for corrosion control are found in the bleach plant. The combination of low pH, dissolved chlorides and thiosulfates, and oxidizing conditions can defeat many alloys noted for their corrosion resistance. The industry has embraced FRP construction on a large scale to combat serious corrosivity of these environments.

Bleaching Processes. Chemical pulps and mechanical pulps are brightened in different ways. Temporary brightening of mechanical pulps used in newsprint furnishes is accomplished by exposing the pulp to hydrosulfite bleach. More permanent brightness is achieved by chemical bleaching with chlorine (C), chlorine dioxide (D), hypochlorites (H), peroxides (P) or oxygen (0), usually in some sequential combination as shown in Figure 4. Between bleaching stages, the pulp is washed, exposed to an alkaline extraction (E) of bleaching residues and washed again before the next bleaching stage. Typical bleaching sequences may be described by acronyms CEDED or CEDHP, to describe the various stages. As shown in Figure 4, multistage bleaching is usually accomplished in bleaching towers, followed by rotary drum washers. Pumps, agitators, and piping are additional components that contact aggressive bleach plant environments.

<u>Corrosion Concerns in Bleaching.</u> The environments encountered in the

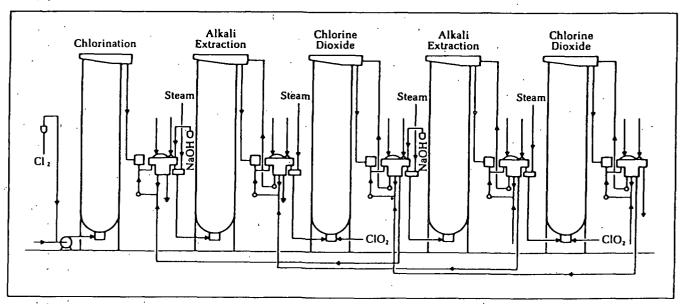
bleach plant are perhaps the most aggressive of those associated with pulp and paper manufacturing. The strong oxidants, low pH values, dissolved chlorides and numerous crevices combine to promote pitting, crevice corrosion and occasionally stress corrosion cracking in all but the most resistant of materials. Consequently, extensive use is made of high molybdenum stainless alloys, FRP construction and, where necessary, corrosion-resistant tile and brick construction.

Chlorine and chlorine dioxide bleach towers are usually lined with acid-resistant brick or tile grouted with silica-rich polyester or silicate mortars.⁹ The carbon steel outer shell is usually protected by a membrane liner between steel and brickwork. Some rubber-lined towers are also in use, and lined pipe is also in common use. In the hypochlorite towers and caustic extraction towers, carbon or graphite brick linings are used for resistance to alkali, with Portland cement or polyester grouts. In spite of the severe corrosivity of the environments in bleaching towers, the linings give acceptable service lifetimes under conditions that would be challenging for most alloys.

Rotary drum washers following bleaching stages are subject to severe conditions, as well. Type 316L may be used for the drum and backing wires, but only if scrupulous attention is paid to preventing Cl₂ or ClO₂ carryover from the towers. Type 317L, with its higher molybdenum content, is now considered to be the minimum level of alloying compatible with bleach plant washers. However, even these highmolybdenum steels may require replacement after five years of service.

Alloys with still higher molybdenum concentrations are finding increasing acceptance for bleach washer service. A recent survey¹⁰ by the TAPPI Corrosion and Materials Engineering Committee indicated that high molybdenum alloys, such as 26Cr-5Ni-6Mo and Ni-15Cr-16Mo-5Fe, are resistant to pitting and crevice corrosion in bleach plant washers, as are the commercial titanium alloys. Care must be taken to use overmatching filler metals to retain the high corrosion resistance of the base metals after welding.¹¹ Although titanium washers are considerably more expensive than washers fabricated from iron- or nickel-based alloys, a few mills have installed these washers and found virtual immunity to pitting and crevice corrosion.

Peripheral equipment - pumps, piping, agitators, showers, etc. - must be fabricated from highly resistant alloys, as well. Type 316L and 317L, and their cast equivalents, are minimal alloys for these applications.



Flow Diagram of a Five-Stage Bleach Plant: CEDED

FIGURE 4--Schematic representation of a multistage bleaching process

Many mills have turned to FRP materials to counteract the severe corrosion encountered in rotary washers. More than 250 washer drums have been coated with FRP for corrosion resistance, with one such washer in service for more than 20 years.⁹ In a typical construction, washer drums are coated with polyester or vinyl ester resins reinforced with glass fiber mats. In at least one instance, an entire drum was manufactured by FRP lay-up. FRP is also frequently used for piping, stock tanks, filtrate lines and other peripheral equipment.

Other mills have turned to electrochemical protection methods to prolong the service lifetimes of 316L and 317L drums, using cathodic protection.¹² More than 70 drum washers have been protected (or scheduled for protection installation) by cathodic protection systems that lower the electrochemical potential well below the pitting potential. Although there have been some concerns about anode durability, this approach has been successful in controlling washer drum corrosion at reasonable cost.

Papermaking

Papermaking Processes. Paper webs can be formed and the water removed in numerous ways, and many different approaches are used depending on the final product. Paper and board are usually formed on a fourdrinier machine with a dryer section as shown in Figure 5, while tissue products are usually dried on a large Yankee dryer cylinder. In both cases, a sheet is formed by feeding a low consistency pulp slurry onto an endless moving screen. Water is removed through the screen at various locations until the web is consolidated sufficiently to transfer it to an endless felt for further drying. Subsequent drying occurs by mechanical pressing in various roll nips, some of which may involve suction applied to the web through perforated rolls (suction rolls). Water removal is completed by contact of the paper web with heated roll surfaces.

The solution chemistry of papermaking is very complex, with additives made to the stock solutions for many different purposes. Papermaking stock is treated to improve wet strength, to reduce moisture penetration (sizing), to enhance water removal, to discourage growth of undesirable organisms, to color paper, and to improve overall product quality. Specialty grades may have other treatments for specific product needs. As a result, a "typical" paper machine stock solution cannot be identified.

Most papermaking stock is sized to some extent to improve resistance to water penetration. Rosin size and starch are common sizing agents which require the addition of papermaker's alum to promote precipitation of the sizing compound on the fibers of the paper web as it forms. The addition of alum results in a mildly acidic stock, with pH values ranging from 4 to 6 being typical. In recent years, synthetic sizing agents have been developed which require mildly alkaline conditions for precipitation — a pH of 7.5 would be typical.

Papermaking stock contains other chemical species that are of importance to corrosion resistance in the paper machine. Chlorides and thiosulfates are often present (10-1000 ppm) as by-products of bleaching operations. Biocides — typically chlorination agents or biologically active organic compounds — are added to paper machine stock to discourage growth of slime and other undesirable organisms.

Increasing paper machine closure to reduce effluents is a continuing trend in the paper industry, with implications for corrosion control as well as other aspects of papermaking. Closure, and the recycling of the process waters that comes with closure, has many effects on white water corrosivity. The concentrations of dissolved solids and salts increase with closure and the temperatures rise as well --- to 70°C in some cases. The chloride/sulfate ratio that determines the pitting propensity may also be upset by recycling paper machine waters. Changes in typical paper machine process water due to closure are shown in Table 1.

as chloride and thiosulfate are often present in whitewater. Second, deposits in the form of fiber poultices or orgonic growths promote crevice corrosion. These conditions, when coupled with the mildly acidic paper machine whitewater, can lead to severe pitting and crevice corrosion problems. Thiosulfates (introduced at the 15 ppm level and above with hydrosulfite brighteners) are particularly damaging to stainless steel, as shown in Figure 6. In some cases, where corrosion is particularly troublesome (e.g., the slice lip at the outlet of the headbox), titanium has been used with success.

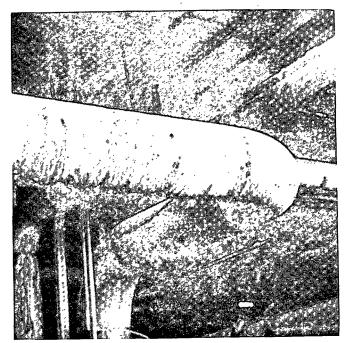


FIGURE 6--Damage to a stainless pipe section (from a stock transfer line) attributed to thiosulfate effects.

Suction roll failures have been particularly troublesome for the pulp and paper industry in recent years. As mentioned in the introduction, Garner has documented more than 190 failures in Canadian mills since 1960. Most of these failures have occurred in widely used bronze and martensitic stainless steels, but failures of austenitic and duplex stainless steels have also occurred. The mechanism of failure appears to be corrosion fatigue.

Increased corrosivity of whitewaters caused by closure may be less of a problem than originally anticipated. Aldrich¹³ reported that only 18% of mills responding to a survey experienced severe corrosion following closure.

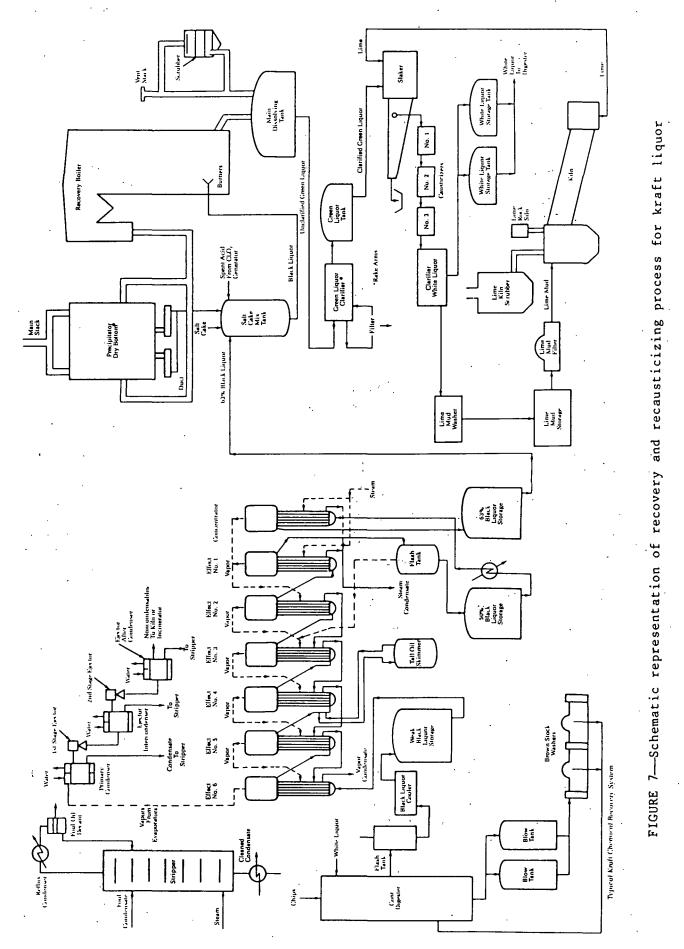
Recovery

Recovery Processes. Recovery of cooking chemicals is important for economic and environmental reasons. In the kraft process, the cooking chemicals are recovered by evaporating the spent liquors extracted from digested pulp, and then burning this liquor in a boiler to make steam and recover the cooking chemicals as molten salts (or smelt) at the bottom of the boiler. These carbonate/sulfide salts are then dissolved and recausticized by contact with slaked lime, followed by clarification to remove the calcium carbonate that precipitates. This process is shown schematically in Figure 7.

Spent liquors are concentrated in multiple effect evaporators made from carbon steel and/or stainless steel (304L or 316L), depending on temperature. At the highest temperatures, the tubes are stainless steel and the shells are stainless clad. In lower temperature effects, carbon steel shells appear, and carbon steel shells appear, and carbon steel tubes are common at the lowest temperature. Occasionally, high rates of corrosion are encountered in carbon steel equipment subjected to vapors or high flows and/or temperatures.

In the recovery boiler, the tubes are usually carbon steel at all locations, but in recent years, some composite tubes have been installed, to eliminate fireside corrosion of the water wall tubes. These composite tubes are coextruded 304 stainless steel (fireside) and carbon steel (waterside). Low superheat temperatures minimize problems with fireside corrosion of carbon steel superheater, screen or generating tubes.

Electrostatic precipitators, used to eliminate entrained sulfates from the flue gases exiting recovery boilers, are subject to severe corrosion when the flue gas temperatures fall below the dew point. The acidic condensates that form are very



aggressive toward carbon steel and concrete in these precipitators. However, stainless steels (316L) and vinyl ester FRP and coatings appear resistant to this attack.

In the recausticizing processes, carbon steel is the typical material of construction, with some use of 304L stainless steel, as well. Carbon steel corrodes at a rate of 20-50 mpy in the kraft cooking liquors, necessitating occasional replacements. Replacement with stainless steel is usually effective in preventing further corrosion problems.

Summary

Pulp and paper mills contain a wide range of very aggressive environments, and a correspondingly large number of materials are used in process equipment to withstand these environments. In a typical mill, carbon steel, stainless steel (304, 316L, 317L), cast iron, concrete and FRP are the "workhorse" materials of construction, but exotic materials such as titanium and duplex stainless steels are used as the need arises. For intractable process conditions, such as bleaching towers and acid coolers, brick and tile construction is used with acceptable lifetimes. In virtually every case, suction rolls being a notable exception, one or more materials have been identified which offer adequate corrosion resistance for the conditions encountered in the industry.

Selection of materials for the pulp and paper industry is a matter of economics, with the most corrosionresistant material not always being the economical choice. Several corrosion control strategies seem to be used (in practice). Some mills choose to use inexpensive materials with marginal corrosion resistance, accepting the fact that frequent repair and replacement will be necessary. Other mills choose to specify the most resistant materials available, in the belief that reduced maintenance and improved runnability offset the higher initial costs. Both strategies are predicated on lowest overall costs, yet the approaches are quite different.

While the pulp and paper industry has traditionally been receptive to new materials of construction, the industry today faces no insurmountable materials problems that await development of new materials. Furthermore, as discussed in the next section, it does not appear that imminent changes in the industry will demand new, more exotic materials for successful implementation of new processes. Instead, it appears that the best opportunities for development of new materials for use in the pulp and paper industry rest with development of alternative materials with adequate corrosion resistance, but with a cost that is attractive compared to current costs of repeated replacement of existing alloys.

TRENDS IN MATERIALS USAGE IN THE INDUSTRY

How will developments over the next decade affect the pattern of materials use in the pulp and paper industry? Will the current strategies for materials selection change because of new processes or changing economic conditions? Are new processes going to require materials with greater corrosion resistance than is currently available?

It should be recognized that the pulp and paper industry is large and mature, and change comes slowly. Capital investment in current processes and equipment will not be discarded lightly. Furthermore, the diversity of products of the pulp and paper industry --- ranging from corrugated board to tissue, from fine papers to nonwoven fabrics --- insulates the industry from revolutionary changes dictated by abrupt changes in market demand. It is fair to say that the industry will be little changed ten years from now, although there will be changes in the product mix.

Although revolutionary changes in the industry are unlikely, there are many evolutionary changes underway that could impact the selection and use of materials in pulping and papermaking operations. Some of these trends are:

> increased mill closure to reduce environmental impact

- concentration of production in large but vulnerable process equipment
- increased running speeds and machine dimensions
- continued upgrading of existing equipment to raise productivity
- concentration of production
- in fewer, larger companies
- controls on labor-intensive
- activities such as maintenance
- evolutionary changes in process chemistry for pulping, bleaching, papermaking and recovery
- lively competition among stainless alloys, fiberreinforced polymerics and electrochemical control methods for controlling corrosion

Each of these trends could have impact on the way materials are chosen and implemented, as discussed below.

Mill Closure

Remarkable progress has been made in reducing the water discharged to the environment per ton of product produced, and this trend will continue. As discussed earlier, closure results in higher temperatures, higher dissolved solids and greater biological growth, all of which have a small but significant impact on corrosivity of white water. With increased closure and recycling of mill process waters, mills may find that materials which performed well for years in the paper machine are no longer adequate and must be replaced by slightly improved materials. For example, 304 stainless steels may be replaced by 316L or 317L stainless steels to achieve desirable performance. Cast iron pump components may have to be replaced with cast stainless steel when fresh seal water is replaced by recycled white water. Based on past experience, the impact of closure will be a modest increase in the failure rate of time-tested materials, with replacement by alternative materials with slightly higher resistance to corrosion.

Closure can lead to unexpected materials problems outside the paper machine area, as well. For example, closure has resulted in higher levels of chloride and potassium in concentrated liquors burned in recovery boilers, to the detriment of superheater tubes now exposed to molten eutectic salts. Environmental restrictions have also limited the use of zinc hydrosulfite brighteners because of concerns about heavy metal ion discharge. The switch to sodium hydrosulfite has been accompanied by a rash of corrosion-related problems, perhaps as a result of eliminating the inhibitive zinc ions.

A third impact of closure is the implementation of new and often untried facilities for treatment of flue gases and other effluents, with severe corrosion of these facilities a nagging concern. Electrostatic precipitators are a good example of pollution abatement equipment that is subject to severe corrosion damage when acidified condensates appear on colder carbon steel surfaces. Severe corrosion has been experienced on walls, access doors, wet bottom trays, expansion joints and feed-throughs fabricated from carbon steel or concrete. Improved materials - 316L stainless and vinyl ester coatings --- appear to have adequate resistance to this environment.

Thus, mill closure is likely to produce a modest effort to upgrade existing materials of construction, but existing alloys are adequate for corrosion resistance under complete closure conditions. A possible exception is the need for more durable suction roll materials, particularly in newsprint mills.

Large, Vulnerable Equipment

Until the late 50's, pulp and paper production at any mill was distributed among several small process systems with considerable redundancy of equipment. A mill would operate many batch digesters at once, as well as three or four small paper machines. If one of these units required repairs, the entire mill was not crippled by downtime taken on one of several redundant production units. In recent years, the equipment has grown larger and continuous processing is more common, so mills are reliant on one large continuous digester or one large paper machine for the bulk of production. While there are considerable economic incentives to increase the scale of process equipment, the large, one-of-kind facilities increase vulnerability to serious loss-of-production costs in the case of downtime on the large equipment. The trend toward larger, more efficient but more vulnerable process facilities is likely to continue.

The increased risk of costly downtime on one-of-kind equipment may influence the materials selection strategy adopted by mills. While redundant equipment could be easily isolated for repairs, repairs to one-of-a-kind components may involve loss of production costs that outweigh the initial costs of more expensive, corrosion-resistant materials. Consequently, there is likely to be a trend toward specification of fully resistant materials --even to the point of over specification --- to insure that corrosion damage will not jeopardize operation of critical equipment.

Increased Speed and Dimensions

As process equipment grows larger and faster, the potential for corrosion damage --- particularly corrosionassisted cracking --- increases as well. Suction rolls are a case in point. Wider paper machines impose greater span widths between roll supports, thereby raising the bending moments and associated stresses. Higher running speeds not only impose more cycles on a roll in a given length of time, but the nip loads are also raised to remove moisture from the web in a shorter dwell time. These factors combine to increase the severity of fatigue loading on vulnerable suction rolls, which may be offset by increased reliance on materials of construction with greater inherent resistance to corrosion damage.

Rebuilding

Although green-field mill start-ups

have been rather rare in recent years, there is considerable activity in the industry to upgrade existing facilities to increase productivity. In each of the last four years, for example, more than six billion dollars was spent by the industry in capital improvements, but only two new mills were under construction.¹⁴ Most of this expenditure is associated with rebuilding and expanding existing mills to achieve higher productivity and a competitive operating position.

The implication of this high level of capital investment is that there are continual opportunities for implementation of new and attractive materials, in spite of a climate where few new mills are justified. The industry would be quick to respond to new materials of construction, provided there are economic incentives for their use.

Fewer, Larger Companies

The proposed acquisition of St. Regis by Champion International to form the largest paper company in the world is the most striking example of a trend in the industry — the concentration of production in fewer, larger companies. Mergers and acquisitions are reducing the number of small paper companies. Half of the paper products manufactured in the United States last year were produced by the ten largest companies; two-thirds of the production is now concentrated in the twenty largest companies.

As a consequence, materials selection decisions are likely to be made with greater input from corporate research/engineering personnel that specialize in corrosion and materials. This scrutiny of the materials selection process will influence the choice of materials. Equipment vendors and materials suppliers can also expect greater sophistication in quality assurance demands by mills. Whether the input of corrosion experts results in greater reliance on highly alloyed materials or an increased dependence on alternative materials such as FRP, coatings, etc., remains to be seen.

Decreased Overhead

The index relating industry production per manhour has been steadily rising in the pulp and paper industry, with productivity increases of 20% in the past six years. Less labor is required to manufacture a ton of product. Accompanying the trend toward lower manpower requirements is the recognition that repair and maintenance activities are often more costly than specifying materials with higher initial cost but adequate corrosion resistance. With fewer hourly workers available for maintenance/repair activities, a premium will be placed on choosing materials of construction that will not require repetitive maintenance.

Higher Yields

In conventional chemical pulping, approximately half of the raw material in wood is retained for use in papermaking; in mechanical pulping, the fraction of wood retained for papermaking is much higher — approaching or exceeding 90%. Increased utilization of high yield mechanical pulping methods will maximize the amount of product available from limited and expensive wood resources. Therefore, reliance on high yield pulping is likely to accelerate in the coming decade.

This is an important trend from a materials viewpoint, because mechanical pulping methods are generally much less corrosive than chemical methods. As this trend continues, there will be less reliance on highly alloyed materials and an accelerated trend toward use of FRP and moderately alloyed stainless steels (apart from refiner plates and some other very specialized equipment).

Evolutions in Processing

The processes used in pulping and papermaking are in a continuous state of flux, as companies experiment to produce products with improved properties at lower costs. For example, some changes that seem imminent within the industry include oxygen bleaching, anthraquinone pulping, sulfur-free pulping and higher sulfidity kraft pulping. These and other changes in processing may affect the demand for corrosion resistant materials. Some changes, such as higher sulfidity kraft pulping, seem likely to increase the demand for stainless steel in the pulp mill, whereas anthraquinone pulping is likely to reduce the corrosivity of these cooking liquors. Displacement bleaching will result in greater reliance on titanium in the bleach plant, whereas oxygen bleaching will probably reduce the corrosive nature of bleaching operations.

Thus, although evolution of processes will have an effect on the materials needed by the industry, the net effect in the long-term, in terms of an increased or decreased reliance on sophisticated materials of construction, remains unclear.

Competition Between Corrosion Control Alternatives

The paper industry has traditionally been eager to embrace cost-effective materials in its overall corrosion control strategies. The industry embraced stainless steels as soon as they were available a half century ago, as it accepted FRP construction for critical applications several decades later. More recently, the industry has been eager to use electrochemical methods - anodic and cathodic protection — as part of an overall corrosion control strategy. The lively competition among highly resistant alloys, fiber-reinforced polymerics, and electrochemical protection will probably intensify.

A case in point is the rotary drum washer used in the bleach plant, where severe corrosion has been commonplace and different corrosion control measures have been used with success. The traditional construction — 316L and 317L stainless steel — is often inadequate and leads to frequent repairs. Yet, some mills continue to rebuild with these marginal alloys in the belief that the overall cost is lower than with other strategies. Other mills have turned to more exotic alloys, such as high-molybdenum stainless steel and titanium, as an expensive but apparently permanent solution to corrosion problems in the washers. Still other mills have chosen to control corrosion at that site by resorting to FRP construction — either as a coating over the carbon steel or as a monolithic fabrication. A final solution adopted at more than 70 washers in North America is the use of electrochemical protection by cathodic polarization of the washer drum to forestall pitting and crevice corrosion. Each of these four strategies has its own advantages and disadvantages in terms of cost, reliability and durability, and it may be many years before one approach is acknowledged as best.

This scenario is likely to be repeated with many other critical components in the coming years. Expensive alloys will find increasing competition from alternative corrosion control measures when equivalent protection can be achieved at lower overall cost. Linings, coatings and claddings will also see wider use. As always, the cost of a given measure will prove to be the deciding factor in adoption of a corrosion control strategy.

SUMMARY

Pulp and paper mills suffer from a host of materials degradation problems, but some of the most severe problems faced by the industry are caused by corrosion. A typical mill must cope with an amazing array of harsh chemical environments. In spite of the number and complexitiy of corrosive conditions, materials have been identified which have adequate corrosion resistance in virtually every process chemistry encountered in the mill. In few cases is the industry still searching for a new material to meet the demands of an existing process condition. Corrosion continues as a concern in pulp and paper mills, largely because of the expense of converting a mill to materials of construction with optimal corrosion resistance.

A mill may adopt one of several corrosion control strategies when faced

with a severe corrosion problem that must be addressed. Selecting marginally resistant alloys and rebuilding as necessary is a time-honored practice in the industry. Specification of fully resistant but expensive alloys is another alternative, but one that is tempered by realization that a new mill can cost as much as \$1 million dollars per daily ton of product manufactured. Where temperatures permit, FRP construction and the use of coatings and linings is a third alternative, and electrochemical protection provides a fourth. Ultimately, total cost dictates the choice of a corrosion control strategy, but there is increasing realization that other costs are involved beyond the cost of materials alone. Lively competition between different corrosion control alternatives will mark the coming decades.

Evolutionary changes in the manufacture of pulp and paper products will affect the need for corrosion-resistant materials in the coming decades, but the net effect remains unclear. Forces are at work which will either increase or decrease reliance on sophisticated materials, but the increased use of advanced materials is probably favored by the high cost of downtime on large process equipment.

The greatest opportunity for penetration of the pulp and paper market lies in development of materials with adequate corrosion resistance but lower costs. Lower cost materials are more likely to break the cycle of specification of marginal materials followed by periodic replacement. In this regard, the nonmetallic materials appear to have an edge, with lower cost raw materials and better prospects for use as coatings and linings.

REFERENCES

- M. F. Davy, W. A. Mueller, Corrosion Problems in the Pulp and Paper Industry, NACE, p. 1, 1974.
- R. Yeske, Pulp and Paper (October, 1983), p.75.
- A. Garner, Proc. 70th Annual Meeting, CPPA (1984) Paper A209.

- 4. Corrosion Problems in the Pulp and Paper Industry, NACE, Vol. 1, 1974.
- 5. Corrosion Problems in the Pulp and Paper Industry, NACE, Vol. 2, 1977.
- Corrosion Problems in the Pulp and Paper Industry, NACE, Vol. 3, 1982.
- 7. Corrosion Problems in the Pulp and Paper Industry, NACE, Vol. 4, 1984.
- K. Jonsson, Handbook of Stainless Steels, D. Peckner and I. M. Bernstein, eds., McGraw-Hill, p.43-1, 1977.

- 9. W. B. A. Sharp, Corrosion Problems in the Pulp and Paper Industry, NACE, Vol. 4, p. 179, 1984.
- 10. A. Tuthill, ibid., p. 133.
- 11. A. Garner, Materials Performance, August, 1982, p. 9.
- L. H. Laliberte, A. Garner, Corrosion in the Pulp and Paper Industry, Vol. 3, p. 329, 1982.
- 13. T. C. Aldrich, R. T. Jones, Tappi J., 56, p. 92, 1973.
- 14. Lockwood's Directory of the Paper and Allied Trades, Vance Publ. Co., New York, 1984, p. 1.

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