Anticipated effects of system closure on corrosion in chemical recovery equipment

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ABSTRACT

This paper reviews literature on parameters that affect the corrosivity of kraft recovery process environments toward commonly-used materials of construction. It discusses the anticipated effects of mill closure on the serviceability of these materials. Although increases in sulfidity and chloride concentration might cause small increases in corrosion rates of carbon steel liquor handling equipment, effects on corrosion rates of the accumulation of nonprocess elements would usually be minor and indirect rather than direct. Accumulation of chlorides and potassium could promote plugging and corrosion in recovery boilers by reducing the first melting point of superheater tube deposits below the temperature of the tube surfaces.

Application:

A literature review shows the factors that affect the corrosivity of kraft liquors and evaluates likely effects of mill closure on corrosion rates of common process equipment materials.

CURRENT EFFORTS TO REDUCE the environmental impact of pulp mill effluents frequently involve reducing the volume of process waters discharged from the mill. Reducing the volume of discharges from the chemical recovery system curtails the discharge of liquors that previously provided a purge of chemicals carried around the liquor system. It therefore increases the concentration of elements and compounds not otherwise removed. As a result, the concentration of nonprocess elements rises to new levels as mill closure proceeds. The final concentration of each chemical will be determined by the rate at which it is supplied to the system, the rate of purge as filtrates and spills are sewered and grits and dregs are landfilled, and the concentration limits at which accumulated chemicals precipitate or change to other chemical compounds.

The accumulation of nonprocess elements affects the corrosion of chemical recovery equipment in three ways:

- Directly changes the corrosivity of kraft liquors
- Produces scale deposits
- Forms corrosive molten deposits on recovery boiler tubes.

This paper will review the parameters affecting the corrosivity of kraft liquors and then evaluate the likely effects of mill closure on corrosion rates of commonly-used equipment materials.

EFFECTS OF MAJOR CONSTITUENTS ON THE CORROSIVITY OF KRAFT LIQUORS

General corrosion in white and green liquors

The primary factors that control rates of general corrosion in white and green liquors are the flow rate, oxidizing power, and temperature of the liquor. Much of our knowledge of corrosion in kraft liquors comes from studies of corrosion in digester environments initiated in Sweden and Canada after the discovery of unexpectedly high corrosion rates of carbon steel digesters during the 1940s. Stockman and Ruus *(1–3)* showed that measured rates of digester thinning were strongly affected by the concentrations of sodium sulfide, sodium hydroxide, and sodium thiosulfate. Christiansen and Lathrop *(4)* fitted Stockman's data to the empirical equation:

$$\text{Corrosion rate } (\mu m/2000 \text{ cooks}) = -91 + 2.8[NaOH] + 0.76[Na_2S] + [Na_2S][Na_2SO_3]$$

(concentrations in grams per liter)

Similar equations have since been developed from data obtained in synthetic liquors *(5)*.

Norwegian research *(6, 7)* explained the dependence of the corrosion rate on the $[Na_2S][Na_2SO_3]$ product by noting that the concentration of these two compounds would determine the equilibrium concentration of sodium polysulfide. Polysulfide ions are strong oxidants. At low concentrations, they accelerate corrosion by consuming electrons liberated by iron dissolution. At high concentrations such as found in polysulfide liquors, they passivate carbon steel. Haegland and Roald *(6, 7)* concluded that the corrosion rate of carbon steel in conventional kraft liquors is determined by the rate of arrival of polysulfide ions at the steel surface.

Other studies *(5, 8–16)* have since confirmed that increases in the concentration of thiosulfates in synthetic white liquors increase the corrosion of carbon steel if thiosulfate concentration remains below approximately 25 g/L *(15)*. Larger concentrations of thiosulfate form a passive surface oxide on the steel that stifles further corrosion. This is

consistent with Ahlers' observation that the corrosion rate of carbon steel digesters used for polysulfide pulping is very low *(13)*. It also agrees with observations by Uusitalo *(17, 18)* and Hassler *(8)* that corrosion rates are lower when iron polysulfide (FeS_2) corrosion products form compared to iron sulfide (FeS) corrosion products forming.

White and green liquors are particularly corrosive at the air to liquor *interface (19)* where inleakage of air raises the thiosulfate concentration. Polysulfides *(20)* and transition metals catalyze this production of thiosulfates from sulfides. Mueller *(21)* has documented increases in the corrosivity of white liquor associated with the formation of thiosulfate catalyzed by the presence of nickel and manganese ions. Reducing the access of air to dissolving tanks, using floating covers on liquor surfaces, adding chelating transition metals, efficiently removing dregs rich in metals that can catalyze liquor oxidation, and using liquor jets rather than air lances in the slaker or classifiers can minimize increased corrosivity associated with thiosulfate formation *(21, 22)*.

Localized corrosion

Corrosion of carbon steel in white liquor and brownstock vessels frequently concentrates in pits. This pitting may arise from the development of sulfur concentration cells similar to differential aeration cells *(23)*. There are indications in the literature that increases in sulfide concentration can produce active and passive behavior on carbon steel similar to that caused by thiosulfates as discussed above *(15, 24)*. Gupta *(24)* reported that carbon steel suffered pitting at pH 11.5 and 14 in "low" sulfide concentrations but was passive in sulfide concentrations between 900 and 5000 mg/L. At pH 14, pitting was most severe when the concentration of sulfides was 200 mg/L. Salvarezza *et al. (25, 26)* observed pitting in much more dilute ($10^{-2}M$) sulfide solutions where the pitting occurred only at pH below 12. Under these conditions, i.e., when the concentrations of hydrosulfide ions (HS^-) and hydroxyl ions (OH^-) were similar, oxidizing potentials took several hours to incorporate sulfide in the anion lattice of surface oxides *(27)*. They then formed isolated black spots of mackinowite—a form of iron sulfide—over growing pits in the metal surface. When the concentration of hydrosulfide ions was much greater than the concentration of hydroxyl anions, oxidizing potentials produced rapid general corrosion under precipitated mackinowite films *(25)*.

Corrosion in black liquors

Corrosion rates in black liquor environments depend on temperature, solids concentration, and the nature of the organic extractives from the wood species being pulped *(28)*. One usually associates corrosion of carbon steel equipment with pitting in neutral or acidic liquids trapped under porous barnacles of precipitated rust, with the addition of acidic filtrates such as shower water, or with condensation of organic acids on the underside of tank roofs *(29)*.

FACTORS AFFECTING CORROSION IN RECOVERY BOILERS

This author has recently reviewed the nature and origin of the species that control corrosivity in eight chemically distinct environments within black liquor recovery boilers. Therefore the selection of materials of construction resistant to these environments will not be repeated here *(30)*.

EFFECTS OF THE ACCUMULATION OF TRACE CHEMICALS ARRIVING WITH THE WOOD

Iron

One would expect the accumulation of dissolved iron arising from liquor system closure to promote the deposition of rust barnacles in brownstock filtrate tanks. As the barnacles form, the pH of the liquid trapped underneath them falls. Pitting can then proceed independently of the composition of the bulk liquor. Regular removal of barnacles by high-pressure water blasting retards pitting damage. The barnacles appear to take many months to form.

Nickel and manganese

The accumulation of nickel and manganese ions catalyzes the oxidation by inleaking air of white liquor sulfides to thiosulfates *(21)*. This effect, however, should not significantly alter corrosion rates of process equipment by kraft liquors. This is partly because many bleached pulp mills are introducing chelating agents to remove metal ions that would decompose peroxide bleaching solutions and partly because efforts to reduce air emissions also reduce air inleakage.

Vanadium

A recent case history of recovery boiler corrosion *(31)* proposed that high vanadium contents in dust deposits that catalyzed the conversion of SO_2 in the flue gases to SO_3 may have promoted the formation of corrosive acidic sulfate deposits on the surface of superheater tubes *(32)*. If the proposed mechanism is correct, the accumulation of other transition metals also may promote the formation of acidic sulfates on water-filled tubes in the recovery boiler upper furnace and economizer sections.

Calcium, magnesium, aluminum, silicon, and barium

Evaporator tubes and liquor boxes particularly in the hotter effects typically use stainless alloys *(33)*. The evaporation processes leave scales on these alloys that are usually either calcium carbonate—with very low solubility—or sodium sulfate-sodium carbonate double salt—with slightly more solubility—that precipitates from black liquor when the solids

content exceeds about 50% *(34)*. Warnqvist has reported that carbonates precipitate from black liquor where calcium concentrations exceed the range 0.1–0.25 g/L *(35)*. Oxalates precipitate at locations where the pH suddenly increases. Evaporator scaling reduces throughput and increases steam costs. The chemical removal of scales can corrode or etch the tube surfaces and thus promote future deposition. Some mills use internally electropolished tubes to minimize scale deposition *(36)*. If scales eventually develop on these tubes, only chelant cleaners should be used to clean them, however, because acids would etch their polished surface.

One would expect rates of evaporator scaling to rise as the concentrations of calcium, magnesium, aluminum, silicon, and barium increase from mill closure. Although scaling reduces production capacity and increases steam costs in the evaporators, note that it also inhibits corrosion on metal surfaces covered by scales in other parts of the liquor system. To maximize equipment life in closed mills, scale removal treatments must be carfully chosen so that they do not attack equipment surfaces. The cleaning chemicals must be appropriate for the equipment materials concerned, suitable corrosion inhibitors must be added, and corrosive residues—particularly those including hydrochloric acid—must be thoroughly flushed from the system *(37)*.

Potassium

The accumulation of potassium in kraft liquors resulting from system closure does not affect corrosion rates of carbon steel in kraft liquors *(38)*.

Organic acids

Condensation corrosion on the roofs of carbon steel tanks could be expected to increase as the concentration of organic acids in the liquor increases. Tonsi-Eldakar has noted that some organic extractives in black liquors would probably accelerate corrosion processes while others would probably inhibit them *(28)*. There is no clear explanation of the net effect of these organic extractives on the corrosion of equipment immersed in black liquor, however. It therefore is not known what effect their accumulation will have on corrosion rates. This author speculates, however, that any effects will be less significant than those associated with the accumulation of inorganic constituents.

EFFECTS OF THE ACCUMULATION OF PROCESS CHEMICALS

Sulfur compounds

If reducing the volume of mill effluents involves the recycling of sulfur bearing wastes—such as end liquor from ClO_2 generation or brines from tall oil processing—into the liquor system, it will raise the sulfidity of the liquors. According to the empirical equations of Christiansen and Lathrop *(4, 5)* and others, increases in liquor sulfidity should produce corresponding increases in rates of general corrosion of carbon steel. Wensley and Charlton *(39)* have related within a given mill gradual and seasonal changes in the corrosivity of white liquor toward carbon steel to changes in the liquor composition. Systematic increases in corrosion rate during the monitoring period corresponded to deliberate efforts to raise the sulfidity of the liquor.

Reports of the effects of sulfite ions are inconclusive. Roald *(7)* and Kesler and Bakken *(40)* suggest that corrosivity decreases with increasing sulfite concentration. Mueller contends that sulfites have little or no effect *(41)*.

Although Yeske reports that minor constituents of kraft liquor do not directly affect the caustic stress-corrosion cracking behavior of digester steels *(42)*, the concentration of electroactive compounds such as thiosulfate and polysulfide may be important because of their ability to raise the surface potential of the steel into the cracking zone *(29)*.

Acidic filtrates

Efforts to reduce effluent volumes have encouraged some mills to recycle acid bleach plant filtrates into the liquor system as brownstock shower water. This approach requires careful evaluation because corrosion rates of carbon steel equipment accelerate substantially if the pH falls below about 10 *(29)* or 9.5 *(43)*. At more neutral pH values, Type 304L stainless steel is necessary for brownstock service. If chloride contents increase as the pH decreases, Type 316L stainless steel may be necessary.

Chlorine compounds

Ahlers *et al. (44)* and Yeske and Garner *(45)* have published useful reviews of the effects of chloride accumulation on kraft recovery processes and equipment. Mueller reported that additions of 0.76–25.3 g/L of NaCl to kraft liquors had no significant influence on rates of corrosion in carbon steel digesters *(41)*. Similarly, the accumulation of chlorides in the closed liquor system of the Thunder Bay mill had little if any effect on the corrosivity of these liquors toward carbon steel or stainless steel equipment *(38, 46, 47)*. Yeske has suggested that one should not expect pitting corrosion in carbon steel and stainless steel in alkaline liquors *(48, 49)* because the easy transport of hydroxyl ions prevents acidification at potential pit sites *(29)* except at crevice sites such as those formed under rust barnacles or mackiowite corrosion products. Yeske notes that chlorides do not cause pitting on carbon steel at pH above 10 *(29)* and do not cause pitting on stainless steel at pH above 12 *(49)*.

KEYWORDS
Accumulation, alkali metals, bibliographies, carbon steel, chemical recovery, chlorides, chlorine compounds, closed systems, construction materials, corrosion, documents, equipment, halides, kraft mills, mills (factories), plant departments, potassium, pulp mills, recovering, review, steel, sulfidity, systems.

High concentrations of chlorides in the liquor cycle will aggravate corrosion in recovery boiler precipitators if and where the temperature of the equipment surfaces falls below the water dew point of the flue gases. Such conditions will bathe the metal surface in mixtures of condensed hydrochloric and sulfuric acids. Carbon steel will suffer catastrophic corrosion, and even Type 316 stainless steel will probably be inadequate *(29)*.

Chlorine compounds and potassium compounds

The simultaneous accumulation of chlorides and potassium in the liquor cycle produces superheater dust deposits with lowered first melting point temperatures *(50, 51)*. This makes the hottest superheater tubes more vulnerable to accelerated corrosion by molten deposits because the corrosion rate of superheater tubes increases abruptly when the first melting point of the dust deposits equals or falls below the surface temperature of the tubes *(31, 44, 51–53)*. Clarke and Singbeil *(54)* noted that careful design and operation of recovery boilers in coastal mills operating with high concentrations of chlorides in their liquor system can avoid high corrosion costs *(55)*.

Both ferritic *(56)* and austenitic *(57)* tube materials may be satisfactory for superheaters operating at temperatures as high as 500°C (932°F), provided the dust deposits are solid. If the dust is molten, however, even exotic high temperature alloys corrode too rapidly to achieve a useful life. In mills where progressive closure may be concentrating chlorides and potassium in the liquor system and lowering the melting point of dust deposits on recovery boiler superheater tubes, careful monitoring is necessary to verify that the surface temperature of the hottest tubes remains below the first melting point of the deposits on these tubes.

The accumulation of potassium and chlorides also makes the smelt in the lower furnace more fluid. Closed cycle operation at the Thunder Bay mill indicates that low melting point temperature smelts do not produce unusual corrosion rates on waterwall tubes *(58)*. However, one would empirically expect increased smelt fluidity to increase corrosion rates of surfaces covered by frozen smelt over which molten smelt is flowing. The increased smelt fluidity should increase rates of heat transfer and therefore reduce the thickness of the frozen smelt layer and increase the metal surface temperature. Others have suggested that this may contribute to the corrosion and cracking of composite tubes in recovery boiler floors *(59–64)*.

EFFECTS OF CURTAILING AIR EMISSIONS

The unplanned oxidation of kraft liquors by inleaking air increases the corrosivity of kraft liquors *(14)*. The oxidizing power of these liquors is sufficient to accelerate active corrosion but not to establish passivity. The installation of black liquor oxidation processes to decrease total reduced sulfur (TRS) emissions, however, produces much greater concentrations of thiosulfate and polysulfide. These are more than adequate to passivate carbon steel *(65, 66)*. Storing black liquor in its oxidized rather than its nonoxidixed form can therefore reduce the costs of liquor storage equipment.

SUMMARY

It is possible to summarize this review of the literature as follows:

1. Accumulation of chlorides and potassium in the liquor cycle can initiate superheater corrosion in high pressure recovery boilers. It may contribute to the corrosion and cracking of composite tubes on recovery boiler floors.
2. To avoid equipment damage, one must carefully control the increased chemical cleaning of evaporators that will be required to respond to accelerated scaling.
3. Accumulation of dissolved iron in the liquor system may accelerate the initiation of pitting under rust barnacle deposits in weak black liquor tanks.
4. Increased sulfidity will probably increase the corrosion of carbon steel process equipment. TJ

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