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Metals Management in the Fiberline

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## METALS MANAGEMENT IN THE FIBERLINE

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### ABSTRACT

Nonprocess element (NPE) concentrations within the fiberline increase as the degree of bleach plant closure increases. Increased concentrations of calcium and barium can lead to scale deposits on process equipment requiring costly downtime to remove the deposits. Increased concentrations of manganese and iron catalyze the decomposition of hydrogen peroxide leading to reduced bleaching efficiency and/or pulp strength loss in oxygen, ozone, and hydrogen peroxide stages.

The open chlorine stage of the conventional bleach plant served as a purge for these NPEs and self-managed metals in the fiberline. Elimination of the chlorine stage and/or closure of the bleach plant water circuits requires controlled purges to manage metals within the fiberline.

### INTRODUCTION

Metals managed themselves in the bleached kraft mill fiberline prior to the use of high chlorine dioxide substitution, oxygen-based bleaching, and increased closure of washer filtrates. Prior to the late 1980s, the first stage of kraft pulp bleaching was based on elemental chlorine and operated below a pH of 2.0. The washer filtrates of the conventional chlorine-based bleach plant were often reused in a counter-current fashion within the bleach plant to reduce energy consumption. However, bleach plant filtrates were not recycled to the brownstock fiberline because of their high chloride content. Bleach plant filtrates were sewered and sent to the effluent treatment system prior to being discharged from the mill. The washer filtrate from the low pH chlorine stage served as an excellent purge of nonprocess elements from the fiberline.

Typical bleached kraft mill fiberline metal profiles for Ca, Mg, Mn, and Fe are shown in Figures 2-5. The process flow diagram for the mill is given in Figure 1. The wood furnish to the mill was primarily Douglas fir, and the C-stage was operating with 50% chlorine dioxide substitution. Complete sampling details and data are given in Ref. (1).

The industry has moved away from elemental chlorine bleaching to chlorine dioxide and oxygen-based bleaching to lower the environmental impact of pulp bleaching. Increased

closure of bleach plant filtrates has been possible with this change in bleaching technology as reported by Union Camp with its high consistency ozone bleaching system(2) and by Champion International with its chlorine dioxide based BFR bleaching system(3). These changes in bleaching technology require proactive management of metals in the fiberline to replace the passive management provided by the environmentally obsolete elemental chlorine bleach stage.

### THE METAL TRAP

Recycling acidic bleach plant filtrates to the alkaline brownstock washers can create a "metal trap." The metal trap occurs because under acidic conditions most cations are desorbed from the pulp by ion exchange with hydrogen ions, and under alkaline conditions most of the cations are sorbed by the pulp by ion exchange with hydrogen ions. This sorption/desorption phenomenon between acid and alkaline wash stages results in a buildup of cations within the loop.

The concentration of cations in the filtrate must increase to the level where the amount being carried over with the pulp mat liquor in the bleach washer and the amount being carried back to recovery in the weak black liquor is equal to the amount entering the fiberline from the digester.

The concentration buildup of cations can be controlled by either purging a portion of the acidic filtrate or installing a metals removal process. Purging part of the acidic bleach stage's filtrate results in a lower level of closure and increased pollutant load from the mill. A metals removal process requires additional capital and increased operating costs.

### PROCESS EQUIPMENT SCALING

Process equipment scaling in the fiberline can be a significant problem when bleach plant filtrates are recycled to the brownstock fiberline and the net bleach plant effluent discharges (purges) are reduced.

Barium, calcium, and magnesium can form inorganic and organic deposits that plug fiberline process equipment. Manufacturing costs can increase and product quality can decrease if scaling is not controlled.

#### Calcium

Calcium is typically the nonprocess element (NPE) of highest concentration entering the fiberline at 1000-3000 mg/kg of dry fiber. The other scale inducing elements are typically lower in concentration by a factor of 10 or more. Under alkaline conditions most of the calcium will be bound to the fiber and usually does not cause problems in the brownstock fiberline or in mills with open bleach plants.

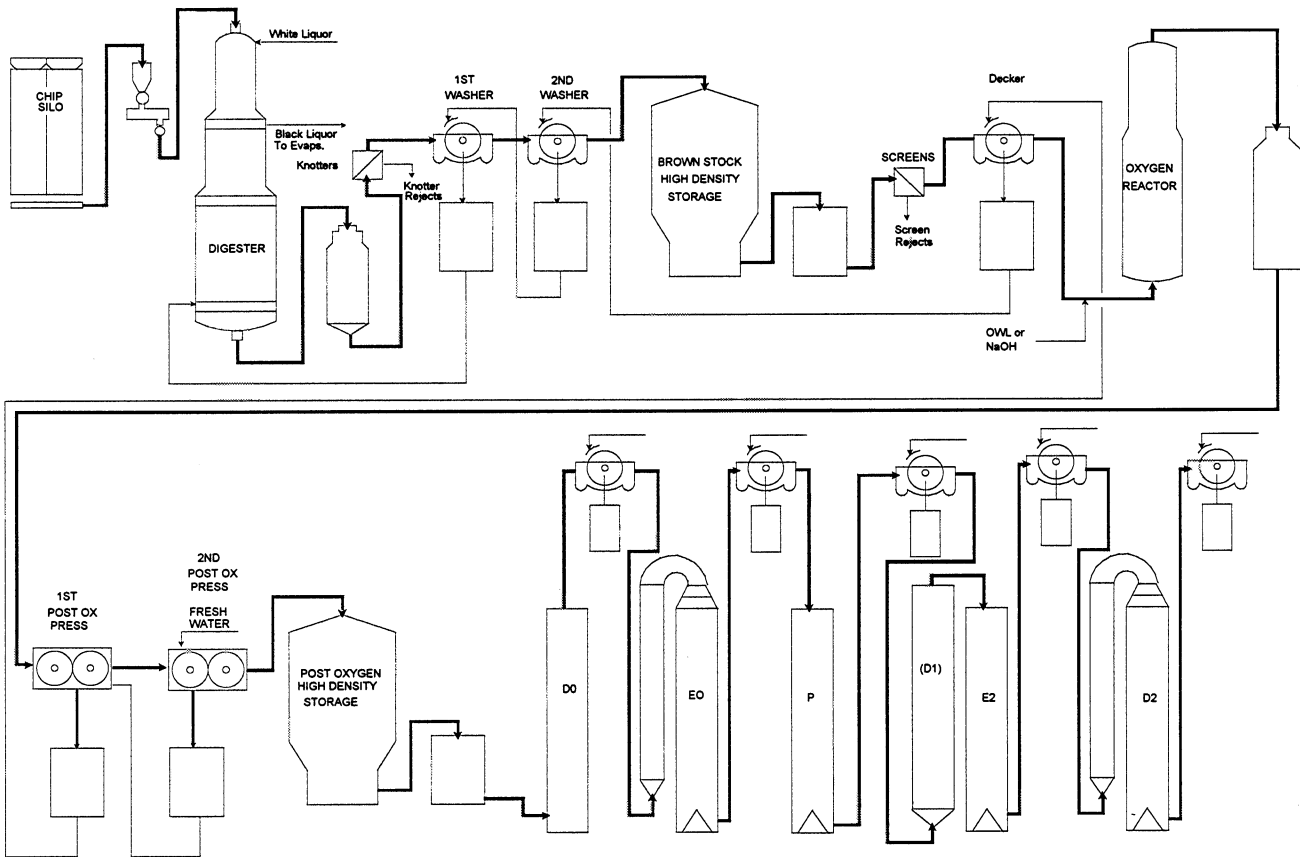


Figure 1. Mill process flow diagram for metal profiles given in Figures 2-5.

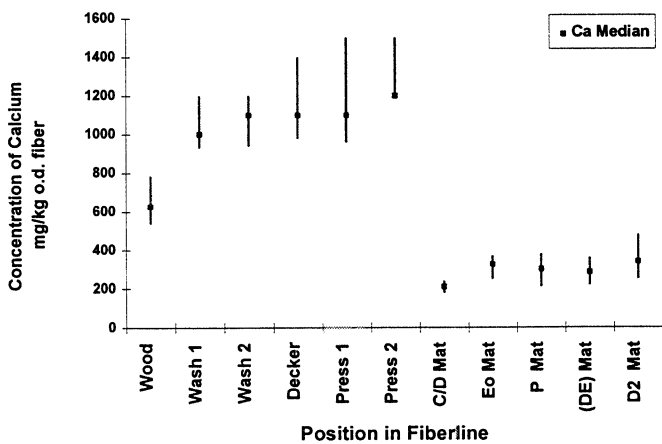


Figure 2. Mill calcium profile. Mat samples analyzed included fiber and mat liquor. Bars represent data range of 10 independent samples collected over a two day period.

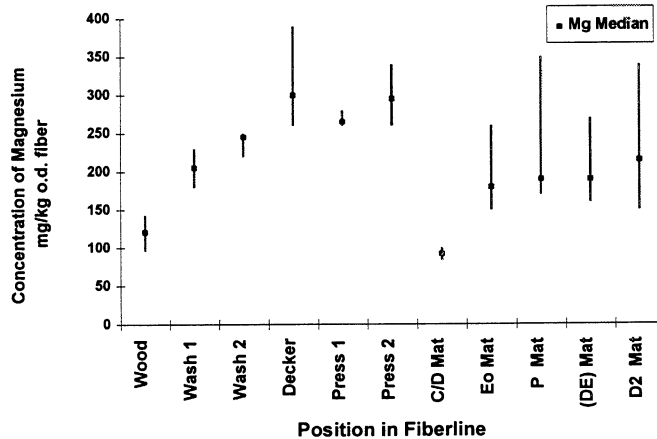
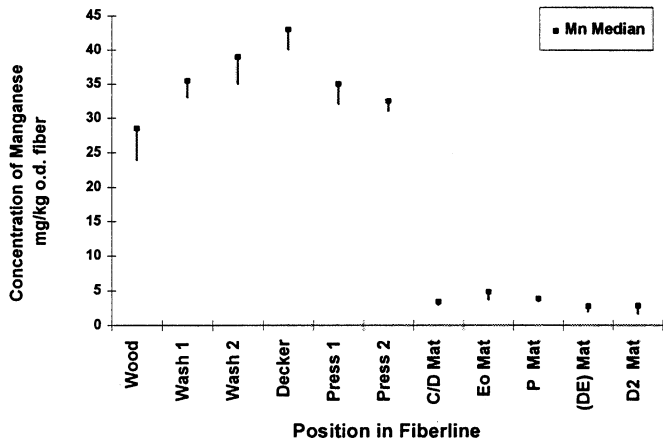
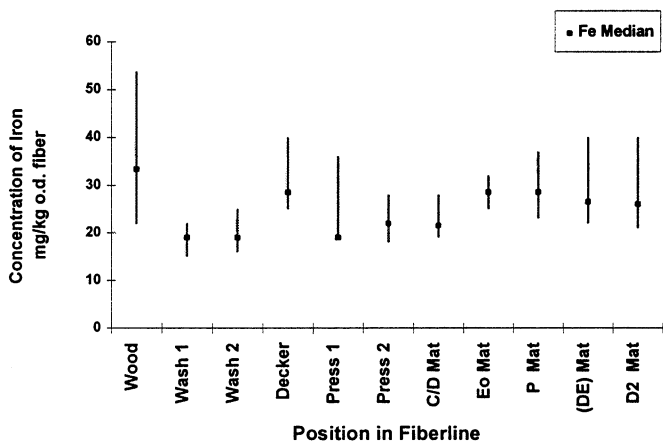


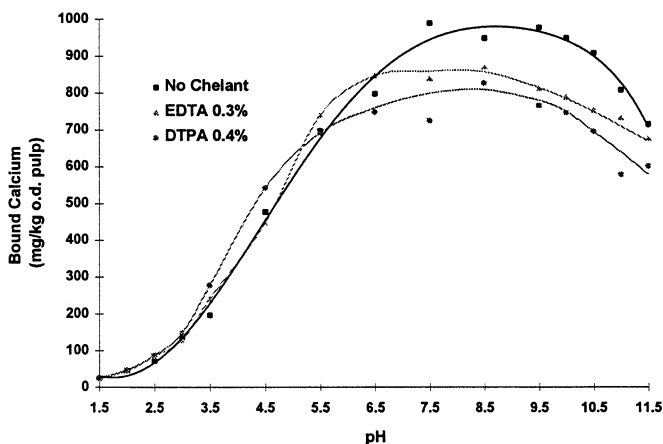
Figure 3. Mill magnesium profile. Mat samples analyzed included fiber and mat liquor. Bars represent data range of 10 independent samples collected over a two day period.



**Figure 4.** Mill manganese profile. Mat samples analyzed included fiber and mat liquor. Bars represent data range of 10 independent samples collected over a two day period.



**Figure 5.** Mill iron profile. Mat samples analyzed included fiber and mat liquor. Bars represent data range of 10 independent samples collected over a two day period.

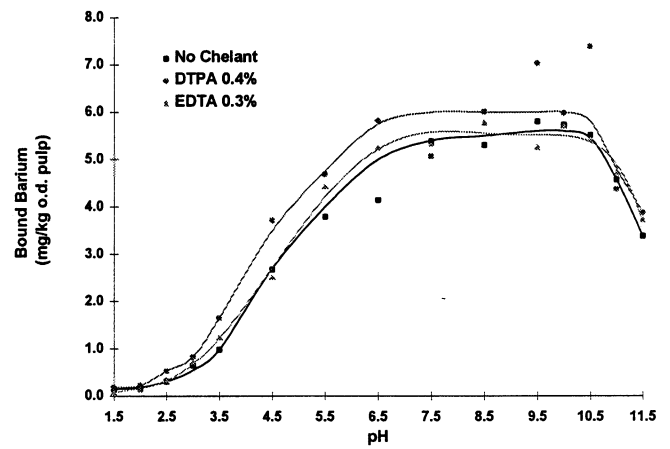


**Figure 6.** Fiber-bound calcium as a function of pH. Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

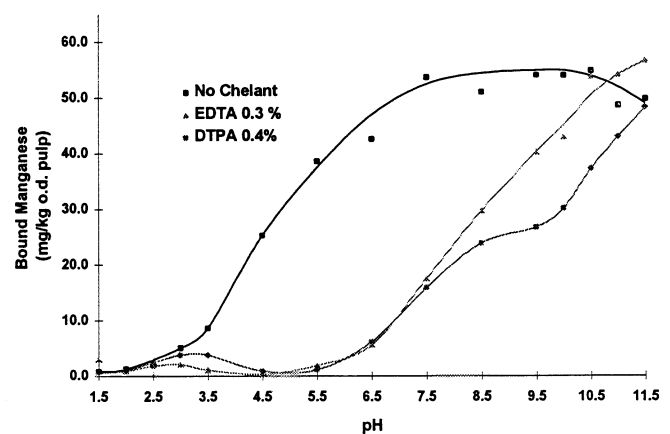
**Figure 6** shows the sorption calcium on unbleached kraft pulp fiber as a function of pH and chelating agent.

Most bleach sequences include at least one acid stage, and many paper machines run under acidic conditions. Closing or recycling acid filtrates back to the alkaline brownstock fiberline results in one or more pH transitions and increased calcium concentrations, which can result in equipment scaling.

Calcium carbonate and calcium oxalate are the two primary alkali-insoluble compounds of concern. Carbonate is formed in pulping reactions and enters as dead load with the white liquor.



**Figure 7.** Fiber-bound barium as a function of pH. Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



**Figure 8.** Fiber bound manganese as a function of pH. Southern Pine 18 Kappa. Temperature 75° C, 1% consistency slurry, 30 minutes mixing.

Oxalate is formed in pulping and bleaching reactions, particularly in oxidative bleaching stages such as oxygen and ozone.

### **Magnesium**

Magnesium is usually 10 times lower in concentration than calcium at 200-350 mg/kg of dry fiber. Magnesium is usually not of great concern when it comes to scaling.  $MgSO_4$  is often added to oxidative bleaching stages as a stabilizer. In high concentrations, magnesium along with other cations can form organic deposits on hot surfaces. Magnesium deposit control is best accomplished by controlling its addition properly.

### **Barium**

Barium is usually 100 times lower in concentration than calcium at 5-10 mg/kg of dry fiber. However, barium forms troublesome sulfate deposits in the bleach plant even under acidic conditions. Sulfate is often in relatively high concentrations in the bleach plant filtrates, since sulfuric acid is often used for pH control. **Figure 7** shows the sorption barium on unbleached kraft pulp fiber as a function of pH and chelating agent.

Barium sulfate deposits have caused operation problems for many mills that recently converted to open ECF bleaching. The typical pH of 2.5-3.5 in  $ClO_2$  delignification stages ( $D_0$ ) is low enough to remove most of the barium from the pulp but not low enough to keep barium sulfate dissolved. The use of hydrochloric acid in the  $D_0$  stage may be a solution for some mills running open bleach plants.

Barium concentrations in the fiberline can be expected to increase as the bleach plant filtrates are closed back to the brownstock fiberline.

### **Oxidative Bleaching Efficiency and Selectivity**

In oxygen, ozone, and hydrogen peroxide bleaching, transition metals catalyze the decomposition of hydrogen peroxide that results in the formation of hydroxyl radicals. The hydroxyl radicals are nonselective and react with cellulose resulting in weaker fibers and lower yields. These metals result in higher manufacturing costs and reduced product quality.

The elements of most concern are Mn and Fe. Co and Cu are also catalytic, but are normally at very low levels (less than 1 ppm on dry fiber). Mg and Ca are important because they help counteract the effects of the transition metals by acting as stabilizers.

Additional organic or inorganic stabilizers can be added to reduce the catalytic activity of transition metals. However, for efficient and selective ozone or hydrogen peroxide bleaching, a metal removal stage is required.

A metal removal stage first desorbs the transition metals from the pulp and then removes them by washing out the filtrate containing the desorbed cations. The overall efficiency of the metal removal stage is a function of both the desorption and the washing. The desorption can be accomplished by either ion exchange or by chelation.

Acid wash stages utilize ion exchange (hydrogen) by acidifying pulp to a pH of 1.5-2.5 followed by washing. Conventional chelation stages (Q-stages) use a combination of ion exchange and chelation by acidifying to a pH of 4.5-5.5 and by adding a chelating agent to provide a competing ligand for the cations.

The two most common chelating agents used prior to hydrogen peroxide bleaching of kraft pulp are ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). Both EDTA and DTPA are more effective under alkaline conditions, but will chelate effectively down to around a 4 pH. Cellulose has a higher affinity (formation constant) for most cations compared to EDTA and DTPA, but has a narrower pH range for effective binding. The conventional Q-stage is operated at a pH between 4.5-5.5 where DTPA and EDTA have a relatively strong affinity for the cations and where hydrogen ions become significant competitors for binding sites on the pulp.

### **Manganese**

Control of manganese is critical for successful hydrogen peroxide bleaching because it catalyzes the rapid decomposition of peroxide. Unlike other transition metals, Mn does not hurt the selectivity of oxidative bleaching reactions because hydroxyl radicals are not formed (4).

The manganese concentration on untreated kraft pulp is typically between 20-150 ppm on dry fiber. In general, it is desired to control the concentration to below 3 ppm on dry fiber. **Figure 8** shows the sorption manganese on unbleached kraft pulp fiber as a function of pH and chelating agent.

### **Iron**

Control of iron is important for oxygen, ozone, and hydrogen peroxide bleaching because it catalyzes the rapid decomposition of peroxides, resulting in the formation of nonselective hydroxyl radicals.

The iron concentration on untreated kraft pulp is typically between 10-100 ppm on dry fiber. There are at least three forms of iron associated with pulp that make it difficult to characterize. **Figures 9 and 10** show the sorption of iron on unbleached kraft pulp fiber as a function of pH and chelating agents for two different Southern Pine pulps that behave very differently.

The first type of iron is a “nonequilibrium” suspended solid. This iron enters the fiberline as dirt with the chips. It can be controlled to some degree by chip washing. The dirt particles can appear small to the naked eye, but are very large relative to ionic dimensions. These particles have a relatively small surface area and are not in equilibrium with the cellulose binding sites. Under alkaline conditions the dissolution of the solid iron is limited by mass transfer and chemical kinetics. The dissolution rate of the solid iron increases with increasing temperature and decreasing pH. Once dissolved, the iron will behave as ionic iron and will be in equilibrium with the binding sites on the pulp.

An apparent increase in bound iron can appear after an acidic bleach stage without additional iron input. The average concentration of the solid iron is often not reflected in the analytical analysis of pulp because of errors associated with taking relatively small samples that may not have evenly distributed solid iron particles. Once dissolved in the acidic bleach stage, the iron is free to ionically bind to the pulp making it easier to detect when analyzing small samples(5).

The suspended solid type of iron is not evenly distributed on the pulp and often shows up as iron concentration spikes when analyzing multiple samples from the same pulp lot (5). Suspended solid iron can also confound a mill steady-state material balance by settling in filtrate tanks and then being swept out as tank levels drop creating transient increases in iron concentrations. Suspended solid iron is catalytically active, but because of its small surface area, it does not play a major role in the decomposition reactions of oxidative bleaching agents.

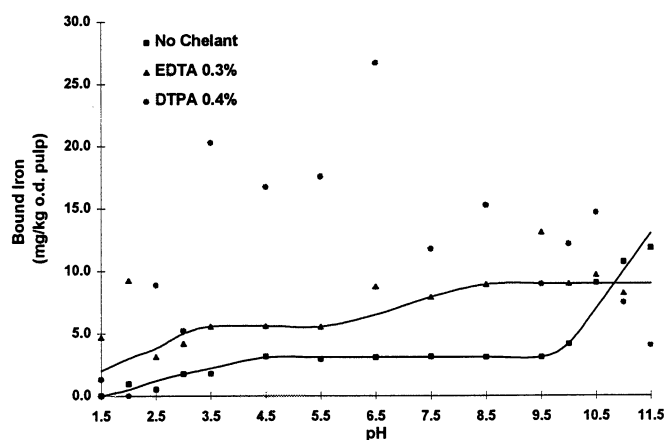
The second type of iron is ionic, either bound or in solution. Further studies are needed to adequately characterize the oxidation state of ionic iron in pulping and papermaking process streams. Ionic iron behaves as other ionic cations and competes for binding sites on pulp or other ligands and can be considered at equilibrium at most points in the fiberline. Ionic iron is highly catalytic and is the iron that must be controlled for oxidative bleach stages. Ionic iron can be removed using an acidic wash stage or by using a chelation wash stage.

The third type of iron is a tightly bound iron. It is unclear if this type of iron is ionically or covalently bound to fiber. This iron cannot be removed by acidic washing or chelation, but is removed with increasing delignification.

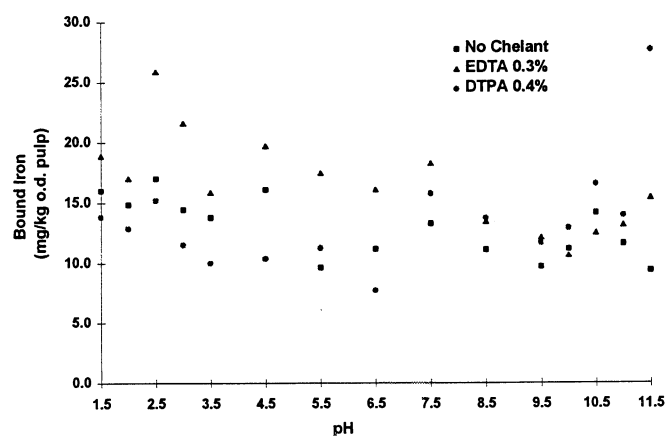
The tightly bound iron is not catalytic and is of less concern than the ionic iron. When the tightly bound iron is removed by delignification, it becomes ionic in nature and is catalytically active.

## Magnesium and Calcium

Control of magnesium and calcium in oxidative bleaching is important because they counteract the negative effects of transition metals. A chelation wash is often preferred prior to a hydrogen peroxide bleach stage over an acid wash stage because it will remove transition metals with a maximum retention of the alkaline earth metals(6).



**Figure 9.** Fiber-bound iron as a function of pH. Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



**Figure 10.** Fiber-bound iron as a function of pH. Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

## PURGES

Conservation of mass requires that eventually the mass of NPEs entering the fiberline must leave the fiberline. In a fully closed-cycle fiberline, NPEs exit with the fiber product, with the weak black liquor, or exit with the aid of a metals removal process often referred to as an "artificial kidney." In a partially closed-cycle fiberline, NPEs may also exit with the sewerer filtrate.

### Filtrate Sewering

Filtrate sewerage is the simplest method of controlling metals within the fiberline, but restricts the level of fiberline closure that can be achieved. The most desirable filtrate to sewer is an acid bleach stage's filtrate because the cations are not significantly bound to the pulp and most of the NPEs are acid soluble. The steady-state filtrate purge required can be determined by a combination of simulation and trial and error. Union Camp uses a filtrate purge in its C-Free high consistency ozone process(2).

Since scale deposition is often excursion based, not exceeding solubility constraints for even short periods of time is often more important than the long-term average concentration. This may lead to a steady-state filtrate purge that is much higher than that required on average. One solution to this problem may be to dynamically control the purge rate by using NPE on-line sensors. In this way, the concentration of NPEs could be controlled while minimizing the rate of filtrate purge.

### Metal Removal Process

Any process that can selectively remove NPEs from the filtrates of the fiberline is a candidate for a metals removal process or an "artificial kidney." There are a number of technologies to choose from, but the challenge has been to find a process that can be economically integrated into our current processes. The dissolved organics and pulp fines in most bleach plant filtrates modify NPE solubilities and tend to foul or plug many separation processes making an economical large-scale separation process technically challenging.

Champion International evaluated both precipitation and ion-exchange as metal removal processes (MRP) for its BFR system(3). Ion exchange was chosen for the initial installation of BFR at Champion's Canton, NC, mill.

### Natural Partitioning Manipulation

Ideally, the metal profile in the fiberline would be controlled by either purging metals from the digester with the weak black liquor (WBL) or purging them at the end of the bleach plant with the fiber.

Forcing cations into the WBL at the digester would require an increase in the relative binding power of dissolved ligands compared to the fiber. This could be accomplished by either increasing the binding power of dissolved ligands (natural or added) or by decreasing the affinity of fiber for the undesirable cations. Once the alkali-insoluble elements enter the liquor recovery cycle, they are purged from the system by dregs removal and the lime cycle purge.

Purging metals with the fiber and avoiding the "metal trap" would require either a completely alkaline fiberline or would require that the cations bind irreversibly to the fiber. Binding cations irreversibly to the fiber could have a significant impact on fiber bonding and final paper properties.

Manipulation of the natural partitioning of NPEs in the fiberline is not economically feasible today. However, current and future research in the industry may lead to economical methods of manipulating the natural partitioning of NPEs.

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