Chemical Additives to Optimize Black Liquor Recovery Throughput and Increase Campaign Life

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ABSTRACT

During normal operation, large deposits can accumulate on heat transfer surfaces of black liquor recovery boilers. These accumulations can result in reduced solids throughput and result in unscheduled outages due to plugging of flue gas passages. Sootblowing and chill and blows can help with deposit removal; however, over time deposits can sinter and become resistant to sootblowing; chill and blows become increasingly ineffective, and ultimately the boiler plugs. Owing to growing demand for kraft pulp, black liquor recovery boilers are often pushed to maximize liquor throughput. As such, recovery boiler operators are challenged to extend campaign life in the face of higher solids throughput. Increased throughput of black liquor solids results in increased carryover, fuming, higher furnace exit gas temperatures, and increased deposition of inorganic salts on heat transfer surfaces, often resulting in rapid deposit growth and plugging. The RECOVERY-CHEM® technology allows operators to maximize black liquor solids throughput by enhancing deposit removal with existing sootblowers, resulting in improved heat transfer, higher boiler thermal efficiency, fewer but more effective chill and blows and an increase in campaign life, that can be extended beyond 12 months between outages. Computational fluid dynamics (CFD) modeling is employed to target chemical injection towards areas in which deposits form, minimizing chemical consumption. Small quantities of slurried magnesium hydroxide are injected to target problem areas (*e.g.* screen tubes, superheater, generating bank tubes). The addition of magnesium hydroxide to the deposit results in efficient deposit removal by existing sootblowers and cleaner heat transfer surfaces. The technology has been successfully applied in black liquor recovery boilers for over twenty years. The technology and performance results will be discussed.

INTRODUCTION

Driven by growth in pulp demand worldwide, long term demand for kraft pulp is projected to increase over the next several years.[1]As a result, kraft pulp mills are often challenged to operate at higher-than-designed black liquor solids throughputs and longer campaigns (*i.e.* time interval between maintenance shutdowns). As firing load increases boiler gas velocities increase, often resulting in increased particle carryover, increased temperatures and increased sulfide flux. Increases in sulfide content and temperatures ultimately can result in greater deposit build up.[2] The combination of mechanical/process improvements and proper application of chemical additives has been demonstrated to be effective in achieving these goals.[3]

Chemical additives have been applied to recovery boilers for several decades to mitigate the fireside deposit accumulation; however, success in deposit mitigation widely varied and results were often inconclusive.[4] Limited success was often due to improper chemical selection, ineffective application (*e.g.* addition directly to black liquor), and poor understanding of operational mechanisms. This paper discusses successful application of magnesium hydroxide slurry, mechanism of operation, and a twenty-year long case history that demonstrates long-term successful control of fireside deposits in a black liquor recovery boiler that operates significantly above the designed dry solids throughput. In this kraft recovery unit, a combination of mechanical/operational changes and targeted application of chemical additives to problem areas has allowed the mill to operate the recovery boiler continuously for 11 months at higher-than-designed throughput without water washing, with the desire to increase campaign life beyond 12 months. The keys to successful application of chemical additives for fireside deposit control and mechanisms of operation are described below.

RECOVERY BOILER DEPOSIT FORMATION MECHANISMS

In kraft recovery boilers, black liquor is injected through liquor guns to distribute black liquor over the char bed. Black liquor droplets are primarily composed of organic lignin-containing residues, Na_2CO_3, Na_2SO_4, NaOH and Na_2S, and proceed through four stages of combustion: (1) drying (*i.e.* water evaporation), (2) de-volatilization of organic matter, (3) char burning, and (4) formation of smelt (Figure 1). Liquor guns inject black liquor with a range of droplet sizes, typically 0.5-5 mm in diameter. During the combustion process, droplets swell during de-volatilization. Huppa *et al*[5] have found that the extent of swelling can have a significant impact on droplet trajectory and droplet burn rate. The result is that small droplets and those that sufficiently swell during de-volatilization can become entrained in the furnace gas stream and carryover towards heat transfer surfaces.

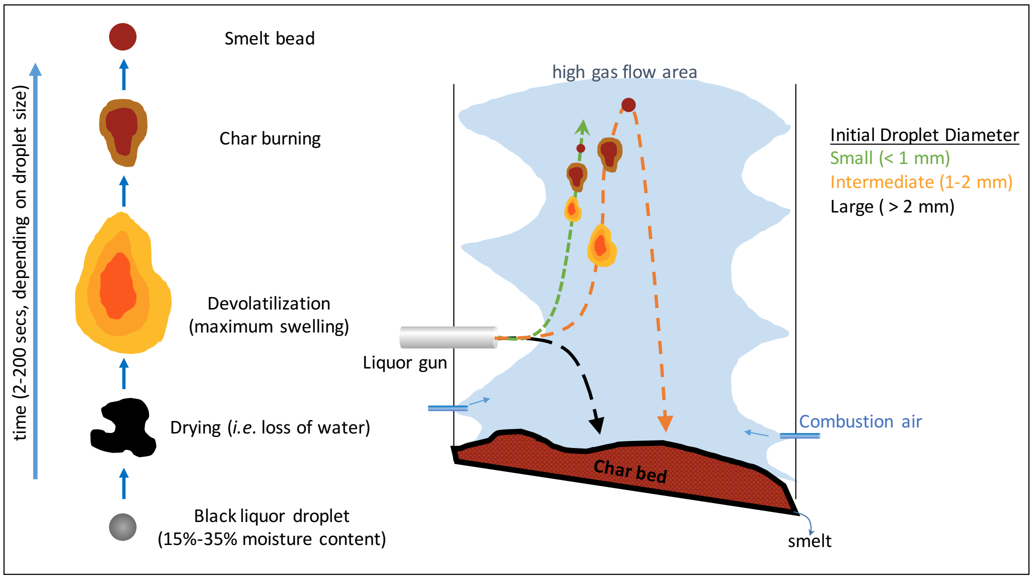


Figure 1. Black liquor droplet stages of burning and impact of droplet size on droplet fate. Black liquor injection through liquor guns results in droplet sizes between 0.5 mm and 5 mm, with a mean size of 2 mm. Droplets burn in four stages: (1) drying (evaporation of water), (2) de-volatilization, (3) char burning, and (4) smelt formation. Small droplets (≤ 1 mm) have lower aerodynamic drag and can be carried upward by gases generated in the furnace (green dashed arrow), intermediate sized particles (1 – 2 mm) swell and can be swept upward or fall back down into the char bed (orange dashed arrow). Large particles (< 3 mm) fall directly onto the char bed and slowly burn (black dashed arrow). (*Figure adapted from Huppa et al*[4])

As firing loads increase (due to increased dry solids throughput), gas velocities and fireside temperatures increase, resulting in increased carryover and fuming rates. At elevated boiler temperatures, the rate of sodium vaporization further increases, and – therefore – the rate of particulate circulation increases.

As carryover and sub-micron fume travel through the furnace, liquid and gaseous sodium salts condense onto heat transfer surfaces (*e.g.* water walls, screen tubes, superheater, reheater/generating bank, etc.) that are below the melting temperature, resulting in deposit build up (Figure 2). Deposits are formed by a mixture of carryover, intermediate sized particles (often called "ISP"), and condensed fume. Most recovery boilers are equipped with numerous sootblowers, installed throughout the furnace, and frequently cycle to remove deposit build up. Sootblowers can be effective at deposit removal; however, at elevated temperatures deposits can sinter and form large, coalesced masses that can be difficult to remove by sootblowing.[2] As sintering deposits continue to grow in size, the growing deposits can reach critical mass and fall, potentially resulting in significant damage to the screen tubes and the lower furnace. Falling slag deposits may break tubes and cause water leaks, and potentially result in initiation of emergency shut down procedures to prevent hazardous water accumulation on the char bed. From a safety standpoint, effective deposit removal by sootblowers limits the risk of large slag falls and tube leaks. From an operational standpoint, effective deposit removal increases the ability to run longer campaigns owing to maintenance of designed pressure differentials (*i.e.* prevention of increase in dP) across various heat transfer surfaces, such as superheater tubes and generating bank tubes.

Several groups have conducted extensive investigations into the mechanisms and chemistry of alkali carryover and fume deposit formation in recovery boilers.[4,5]

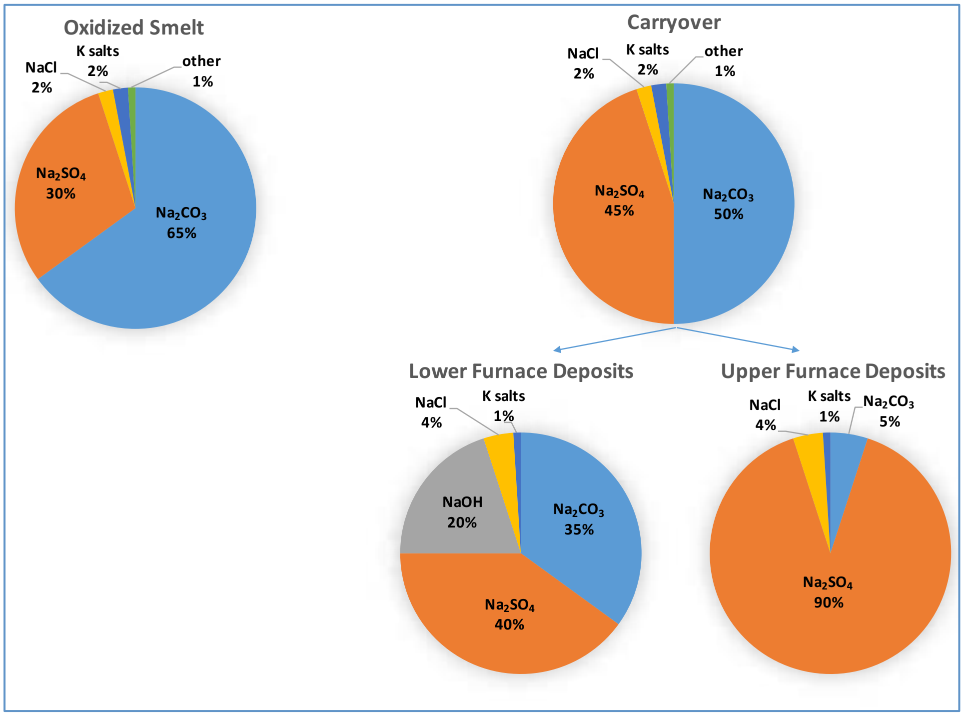


Figure 2. Chemical Compositions of Oxidized Smelt, Carryover, and Lower and Upper Furnace Deposits. (*Adapted from Tran et al*)[2]

CHEMICAL ADDITIVES FOR DEPOSIT CONTROL

Chemical Additives

In an effort to minimize deposit accumulation in kraft recovery boilers, numerous chemical additives have been evaluated over the past several decades, including: $CaCO_3$ (calcite), CaO (lime), $Ca(OH)_2$ (hydrated lime), MgO (magnesite), $Mg(OH)_2$ (brucite), aluminosilicates, such as kaolin, talc, and vermiculite, and MnO_2 (manganese dioxide). Many of these additives have been evaluated in coal- and oil-fired boilers to treat slag deposits; however, the kraft pulping process is sensitive to the introduction of non-process elements (NPEs). Therefore, selection of chemical additives must consider complete balance-of-plant impacts, including impact on chemical cycling in the recovery unit, the green liquor cycle, and the white liquor cycle. As such, calcium- or magnesium-based chemistries are preferred owing to their limited impacts on the kraft recovery process.

Chemical additives can be applied as either dry powders or aqueous slurries of powders. In many applications, additives have been applied directly into the black liquor and sprayed into the the recovery boiler. The RECOVERY-CHEM technology utilizes brine precipitated

$Mg(OH)_2$ with a mean particle size of 1-5 μm, and a native surface area between 13-15 m^2/g that increases to 60-150 m^2/g when calcined to MgO in the furnace. For comparison, natural minerals such as limestone (*i.e.* $CaCO_3$) or brucite (*i.e.* mined $Mg(OH)_2$) are significantly more crystalline than precipitated minerals and have typical surface areas between 1-5 m^2/g, and have typical milled median particle sizes between 5-20 μm. Additionally, in brine precipitated $Mg(OH)_2$, high surface area is derived from low crystallinity, numerous structural defects, and a large number of pores within granules, that fragment into many submicron-sized particles during furnace injection (*i.e.* flash calcination to MgO). This results in relatively high reactivity due to greater distribution per unit mass of chemical applied, and – ultimately – reduced treatment dosages.

Mechanisms of Operation

The mechanisms of deposit mitigation by chemical additives have been inadequately studied and remain poorly understood. Inconclusive results in some units resulted in industry-wide cynicism regarding the efficacy of additives. As a result of twenty years of continuous application in kraft recovery boilers, coal-, oil, biomass-fired boilers, refineries, and waste-to-energy facilities, numerous laboratory, pilot-scale and full-scale studies were conducted to shed light on how $Mg(OH)_2$-based additives work and how to improve efficiencies. The primary plausible mechanisms for deposit control by chemical additives include: (1) increase the deposit melting temperature (*i.e.* increase in fusion temperature), (2) decrease in deposit strength/stability for efficient removal by sootblowers, sonic horns, or impulse cleaners, and (3) reduce the concentration of low melting compounds within deposits (*i.e.* dilution of low melting compounds).

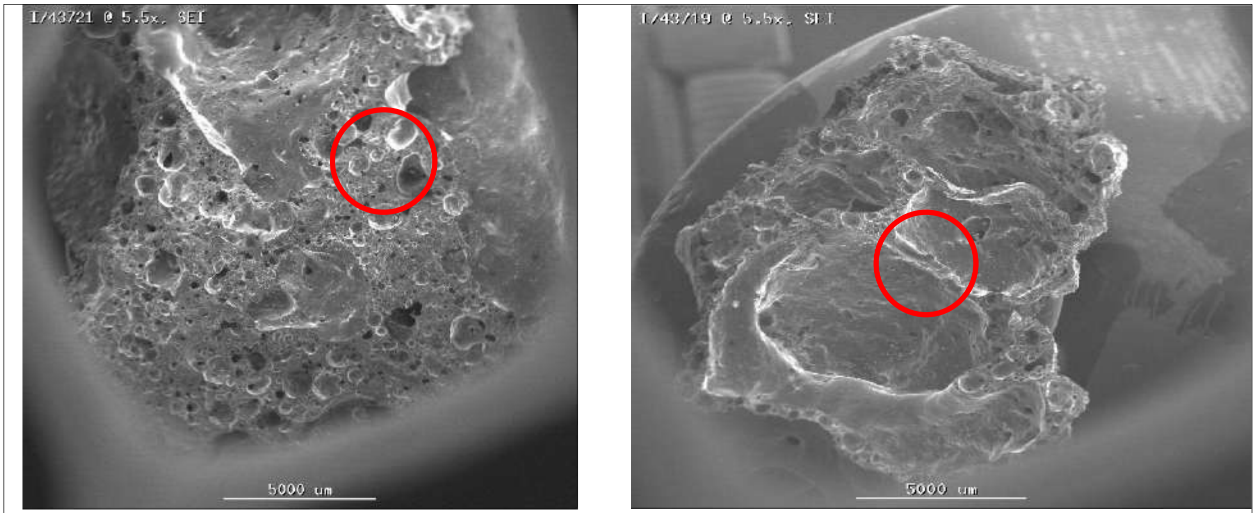
Fate of $Mg(OH)_2$ slurry in furnaces. Magnesium compound injection (primarily as MgO, $Mg(OH)_2$, and $MgCO_3$) has been evaluated in a variety of furnaces, including kraft recovery units. For deposit control, the most effective form of magnesium is $Mg(OH)_2$ injected as an aqueous slurry (typically 60% w/w). At temperatures greater than approximately 325 ^oC (617 ^oF), $Mg(OH)_2$ decomposes to $MgO_{(s)}$ and $H_2O_{(g)}$. Upon injection from room temperature into furnace temperatures, both structural water (*i.e.* originating from hydroxide moieties) and bulk water from the slurry flash evaporate. Under these conditions, hydroxide groups undergo condensation reactions and the $Mg(OH)_2$ structure rapidly decomposes to $MgO_{(s)}$. At furnace temperatures, flash evaporation of structural and bulk water is a relatively violent process that results in significant fragmentation of the original particle into numerous smaller particle fragments. Specifically, brine precipitated $Mg(OH)_2$ slurry is comprised of particles with median sizes between 1.6 μm - 2.3 μm. Upon rapid calcination, $Mg(OH)_2$ particles are reduced to MgO particles with median diameters measured between 0.06 μm and 0.3 μm, resulting in significant fragmentation of the native 2 μm. As such, one 2 μm diameter $Mg(OH)_2$ particle fractures into numerous smaller particles, specifically between 300 x 0.3 μm particles and

37,000 x 0.06 μm particles. The result is that numerous smaller particles are created from individual $Mg(OH)_2$ that are available to disperse through the gas phase and distribute throughout accumulating deposits. To elucidate the underlying mechanisms that govern deposit mitigation by $Mg(OH)_2$, a number of studies were conducted to determine the feasibility of each plausible mechanism.

Impacts on deposit melting behavior. To determine whether chemical additives increase the melting temperatures of recovery boiler deposits, ash fusion tests were conducted on simulated carryover (75% Na_2SO_4, 25% Na_2CO_3). Ash fusion tests rely on pressing powdered samples into a cone and heating the cone to measure deformation and melting behavior (modified ASTM D1857/D1857M). Addition of $Mg(OH)_2$ from 0.1% (w/w) to 1 % (w/w), did not significantly alter the melting characteristics of recovery boiler deposits, even when $Mg(OH)_2$ concentrations were significantly greater than can economically be added to a recovery unit. Therefore, it is unlikely that $Mg(OH)_2$ mitigates recovery boiler slag deposits by chemically increasing melting temperatures. Additionally, it is unlikely that deposits are effectively treated by dilution of low melting compounds within the deposits (*i.e.* by dilution) given that $Mg(OH)_2$ is typically injected at rates between 0.5 lbs/ton and 2 lbs/ton of dry solids, or 0.025% (w/w) and 0.1% (w/w), respectively.

Impacts on deposit strength

To investigate the impacts of $Mg(OH)_2$ injection on the physical characteristics of deposits, deposit samples were collected prior to treatment (baseline) and during chemical injection, from the same heat transfer surface. Figure 3 illustrates the impacts of $Mg(OH)_2$ injection on the physical properties of deposit samples. In this study, deposits were collected from generating bank tubes, before and during $Mg(OH)_2$ injection. Observation of deposit samples using scanning electron microscopy reveals that injection of $Mg(OH)_2$ at low dosages (in this case, 1 lb/ton of dry solids or 0.05 % w/w) significantly altered the pore structure of the generating bank deposits. Untreated deposit samples contained many relatively small pores (300 μm – 1600 μm) that are separated by thick, dense walls The presence of dense deposits with many small pores indicates that as molten droplets condense onto transfer surfaces they sinter.[2] As the condensed particles sinter and anneal, adjacent particles coalesce and densify, resulting in increasingly stronger deposits that are difficult to remove by sootblowing. As illustrated in Figure 3, addition of small quantities of $Mg(OH)_2$ alters deposits by increasing the sizes of pores (2500 μm – 5000 μm). It is possible that the presence of foreign MgO (from $Mg(OH)_2$ injection) particles in molten droplets alters their fluid properties (e.g. viscosity, surface tension) and/or disrupts the extended bond network of the inorganic phases that comprise the solid as droplets condense on heat transfer surfaces, resulting in defects within the solid deposit. As defects and pores within the deposit increase in size, walls between adjacent pores become thinner. As the ratio of pore wall thickness to pore diameter decreases, the deposits become less stable and weaker. As external motive forces are applied by sootblowers, small cracks and fissures can propagate and form cleavage planes. As a result, deposits with large pores and thin walls tend to be weaker and are more easily removed by sootblowers.



Deposit without RECOVERY-CHEM®
Numerous small pores with thick pore walls

Deposit with RECOVERY-CHEM®
Large pores with thinner pore walls

Figure 3. Impact of chemical injection on deposit physical properties. Deposits samples were collected from generating bank tubes and analyzed using scanning electron microscopy (SEM). During baseline (no chemical injection), deposit samples are dense, with many small pores and thick pore walls. $Mg(OH)_2$ injection results in deposits with larger pores and thinner walls between adjacent pores. Thinner walls between pores decrease the strength of deposits, resulting in more efficient removal by sootblowers. Red circles are shown to compare the relative number of pores and thickness of walls between untreated (left panel) and treated (right panel) samples.

SEM provides insight into the microscopic differences between untreated and treated deposits samples. To investigate the impacts of $Mg(OH)_2$ on deposit strength on the macroscopic scale, compression strength tests were conducted on simulated sintered deposits. Figure 4 illustrates the compression strength required to fracture pellets that simulate carryover deposits as a function of $Mg(OH)_2$ addition. As the fraction of $Mg(OH)_2$ increases, the load required to fracture the deposit progressively decreases. Therefore, injection of $Mg(OH)_2$ alters the physical properties of recovery boiler deposits on the microscopic scale. This results in reduced deposit strength on the macroscopic scale, and results in more efficient removal by sootblowers.

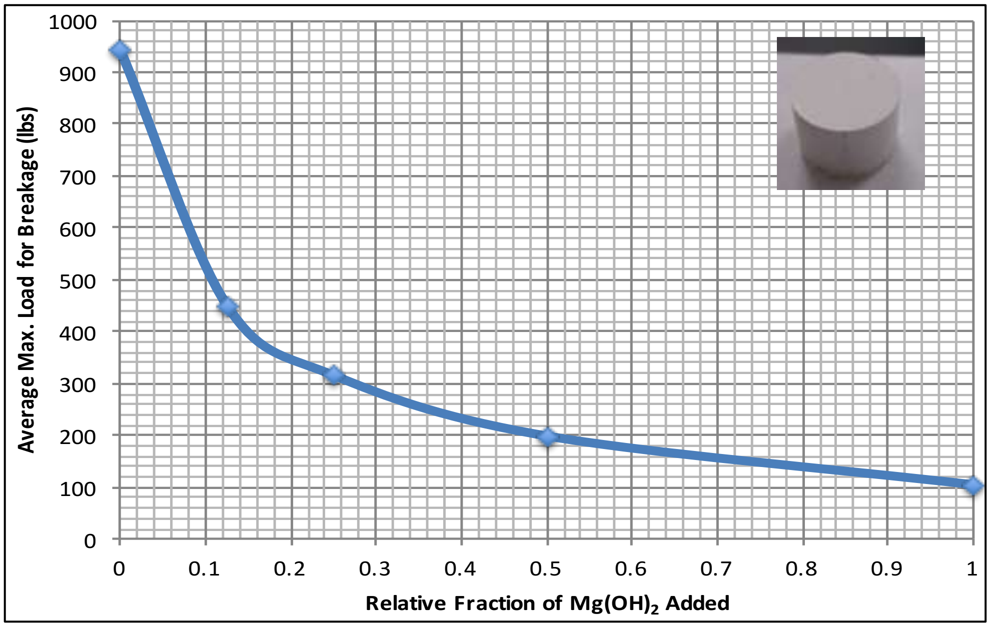


Figure 4. Impact of chemical addition on deposit compression strength. Carryover deposits were simulated by a mixture of Na_2SO_4 and Na_2CO_3, pressed into pellets, and sintered at 775 ^{o}C for 2 hours (see inset). Compression strength tests were conducted in triplicate (on separate pellets) and averaged.

CRITERIA FOR SUCCESSFUL MITIGATION OF RECOVERY BOILER DEPOSITS

Successful treatment of recovery boiler deposits requires: (1) injection of chemical targeted towards problem areas, typically screen tubes, superheater tubes, generating bank and/or reheater tubes, (2) proper selection of chemical injection technology, and (3) efficient application of motive forces to remove deposits (*e.g.* sootblowers, sonic horns, impulse cleaners). Properly applied, the technology allows operators to maximize dry solids throughput by enhancing deposit removal with existing sootblowers. This results in improved heat transfer, higher boiler thermal efficiency, fewer - but more effective - chill and blows, an increase in campaign length, and prevention of dangerous tube leaks that can result from slag falls.

CASE STUDY

Background

Fuel Tech has successfully treated the subject kraft recovery boiler for twenty years. This case history illustrates that the combination of mechanical/operational changes in the recovery unit coupled with proper $Mg(OH)_2$ application allows the mill to operate at significantly higher-than-designed dry solids throughput and campaigns that increased from 90 days (in 1995) to nearly 11 months (in 2015) between water washes. Originally, the mill produced an excess of black liquor, and liquor was trucked to nearby mills. With recovery unit modification the mill was able to increase throughput from a designed 2.4 million lbs/day of dry solids to 4.1 million lbs/day of dry solids. By preventing pluggage at higher solids throughputs, proper application of chemical additives allows the unit to operate for longer periods between outages. The following case study describes the operational modifications and design of the targeted chemical injection system that allowed the mill to operate well beyond design capacities and significantly increasing the mill's profitability.

Mechanical Improvements to Increase Black Liquor Throughput

The subject pulp and paper mill was designed as a nominal 1,050 tons per day bleached kraft pulp mill, utilizing 50% northern softwood and 50% northern hardwood as a prime feedstock. The recovery unit is a B&W boiler, designed originally with a throughput of 2.4 million pounds per day of dry solids throughput. The unit operates at 900 psig and produces steam at a rate of 540,000 lbs/hr. The recovery boiler has a relatively low aspect ratio of 2.7, which results in a tendency for the unit to plug when overloaded. Beginning in the 1980s the recovery unit was pushed to increase throughput beyond design capacity. Consequently, frequent water washes were required to remove extensive pluggage in the generating bank. Additionally, excess black liquor had to be trucked daily from the mill site to nearby mills.

As a result of frequent pluggage and the need to truck black liquor offsite, a number of mechanical and operational changes were instituted throughout the 1990s. In 1991 a standalone high pressure tertiary air fan was installed, additional liquor nozzles were installed, and a new superheater was added to increase the heat transfer surface area. In 1994 a new upper furnace was installed and the unit's tertiary air fan was further upgraded. Additionally, black liquor solids were increased from 65% to 71% as-fired. In 1995 a consumed air strategy was implemented which reduced furnace gas velocities and decreased carryover. These operational changes resulting in the ability to increase the throughput from t2.4 million lbs/day of dry solids to 3.2 million lbs/day of dry solids.

An environmental improvement project was initiated in 1995 and resulted in a requirement to process even greater solids levels, increasing the throughput requirement to 3.5 million lbs/day of dry solids. As a result of the unacceptably frequent pluggage at the desired throughput increase, a trial program using chemical based additives was initiated in late 1994 to minimize pluggage. In conjunction with the use of chemical additives, the mill began an investigation of additional upgrade options for the boiler to increase throughput and decrease deposit formation. Consequently, new drum internals were installed, to increase the steam production capacity to accommodate higher black liquor throughput. Design and installation of a new tertiary air fan to allow a 40% tertiary air split to help reduce entrainment and mechanical carryover was also completed.

In 1996 and again in 1998, several modifications were made to the steam drum internals to allow for the higher steam production rates. Computational fluid dynamics (CFD) modeling was completed in 1998 to aid in the selection of new secondary air dampers to improve air distribution in the lower furnace. In 1998, a continuous SO_2 analyzer was installed which allowed the boiler to be run with low SO_2 emissions. In 2000, partial purging of the precipitator catch was implemented to lower chlorides to minimize corrosion.

Overview: Fireside Additive Program to Minimize Pluggage with Increased Black Liquor Throughput

In 1995, application of the RECOVERY-CHEM program was initiated and optimized, prior to installation of the new tertiary fan design and associated firing strategy was implemented. At the beginning of the chemical additive program evaluation, the recovery unit was able to operate for 3 months between water washes (Figure 8), required frequent thermal shed procedures (*i.e.* "chill and blows") and needed four to six truckloads of liquor taken off site per day.

The use of a targeted chemical injection program coupled with optimized firing techniques like perimeter firing has resulted in a steady increase in solids loading, elimination of liquor trucking, and a boiler capable of running longer between water washes. Today, the recovery boiler averages 4.1 million pounds per day dry solids fired. Normal campaign runs are between six and nine months in duration, with a recent completed run of eleven months. The mill has expressed strong interest in investigating the possibility of campaign runs up to 18 months in duration.

At the start of the chemical injection demonstration period in 1995, the mill fired 3.2 million lbs/day of dry solids in their recovery boiler and experienced severe superheater and generation bank fireside fouling. Each successive chill and blow was less effective than the previous one due to hard slag breaking up and chunks landing on top of the mud drum. This slag would aggregate and result in draft fan load increases due to the physical obstruction to gas flow. This slag buildup also resulted in production shutdowns caused by the increasing pressure differential that prevented the unit from achieving the desired dry solids throughput.

Prior to 1995, the mill evaluated several chemical additives that were directly added to the black liquor, with poor results. In contrast, targeted injection of $Mg(OH)_2$ slurry to areas in the furnace in which deposits historically formed, instead of targeting the fuel, resulted in significant improvements in deposit mitigation performance and cost effectiveness. In targeted chemical injection, the additive application is "aimed" at the problem heat transfer surfaces, so that the vast majority of chemical goes to the problem areas instead of with the flue gas to the precipitator. As a result, even at low injection rates, the local MgO concentration in the deposit is likely great enough to modify the physical properties, as was described above, for efficient sootblowing. Targeted chemical application requires detailed furnace modeling and advanced chemical injector technology to be employed.

CFD Modeling and Targeted Injection Strategy

The first step to targeted injection of chemical additives is to model the recovery unit with inputs that include: boiler geometry, heat rate, fuel flows, fuel composition (for all wood species and blends thereof), primary, secondary, tertiary (and quaternary) air flows and splits, temperatures, heat transfer surfaces, moisture input, and boiler geometry are programmed into the model. From these inputs, the recovery unit gas flow dynamics (*e.g.* vectors, velocities, recirculation zones, etc.) and temperature profile are computed. A comprehensive combustion survey is conducted to gather all of the required inputs to model the recovery unit. Spot flow and temperature measurements are used to tune and validate the CFD model. Figure 6 illustrates the gas flow dynamics of the subject recovery boiler and parameters required for successful application of $Mg(OH)_2$ for deposit control.

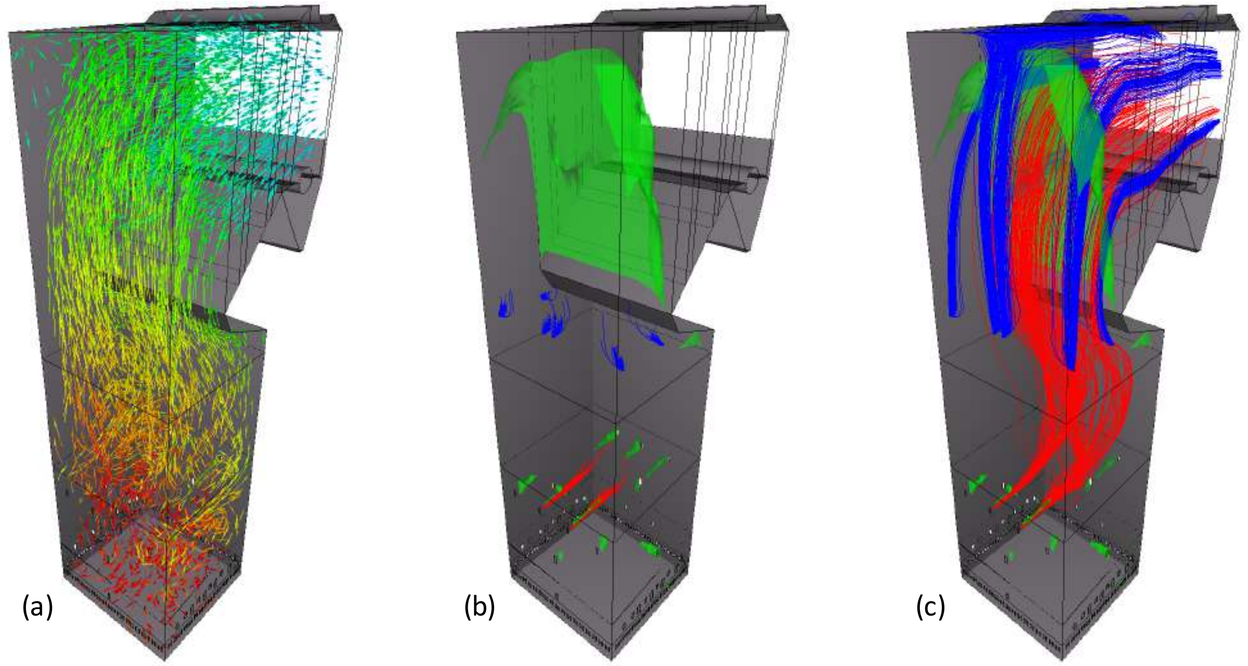


Figure 5. Computation fluid dynamics (CFD) model of a black liquor recovery boiler and chemical injection. (a) Boiler operating conditions were modeled for black liquor derived from hard and soft wood species. Primary, secondary, and tertiary air flow rates were included. Colored arrows depict gas flow velocity vectors, and are colored according to temperature. Modeling recovery boiler gas flow dynamics is the first step to identifying an injection strategy for deposit control. (b) Once gas flow dynamics are modeled and problem areas are identified, virtual injectors are placed in various locations within the boiler. Streamlines that emanate from injector tips represent water droplet lifetimes (to complete evaporation). The green surface represents the melting temperature isosurface of recovery boiler carryover, (c) Trajectories of particles are modeled as having zero mass and infinite drag to determine the directionality of small particle flow. The injection strategy is optimized to achieve targeting of problem areas within the recovery unit.

Once the recovery unit's fluid dynamics are computed and the model is validated, the next phase of the modeling involves identification and optimization of a chemical injection strategy. Historical recovery unit deposit surveys and predictions from the CFD model are used to identify problem areas, and provide initial targets for chemical application points. To that end, injector type, injector settings, and injector location are varied to produce individual scenarios, and resultant chemical coverage maps are calculated. In this unit, deposition primarily occurs at the inlet of the generating bank, with deposit formation beginning along the side walls and builds towards the top of the furnace and into the center. Initial injector locations are selected to maximize the use of existing view ports, doors, and/or air ports, and other existing penetrations on the unit. Figure 6 illustrates the results of three injection strategy cases. Streamlines that begin at the injector tip represent water droplets. These streamlines end when evaporation is complete and the chemical is calcined and activated. Chemical coverage contour maps are colored by relative concentration, with cold colors (black, purple, blue) indicating lower concentrations and warm colors (green, yellow, red) indicating high concentrations. In this unit, the goal was to achieve uniform coverage across the entire inlet to the generating bank, with slightly higher chemical concentrations at the side walls, where deposition is heaviest.

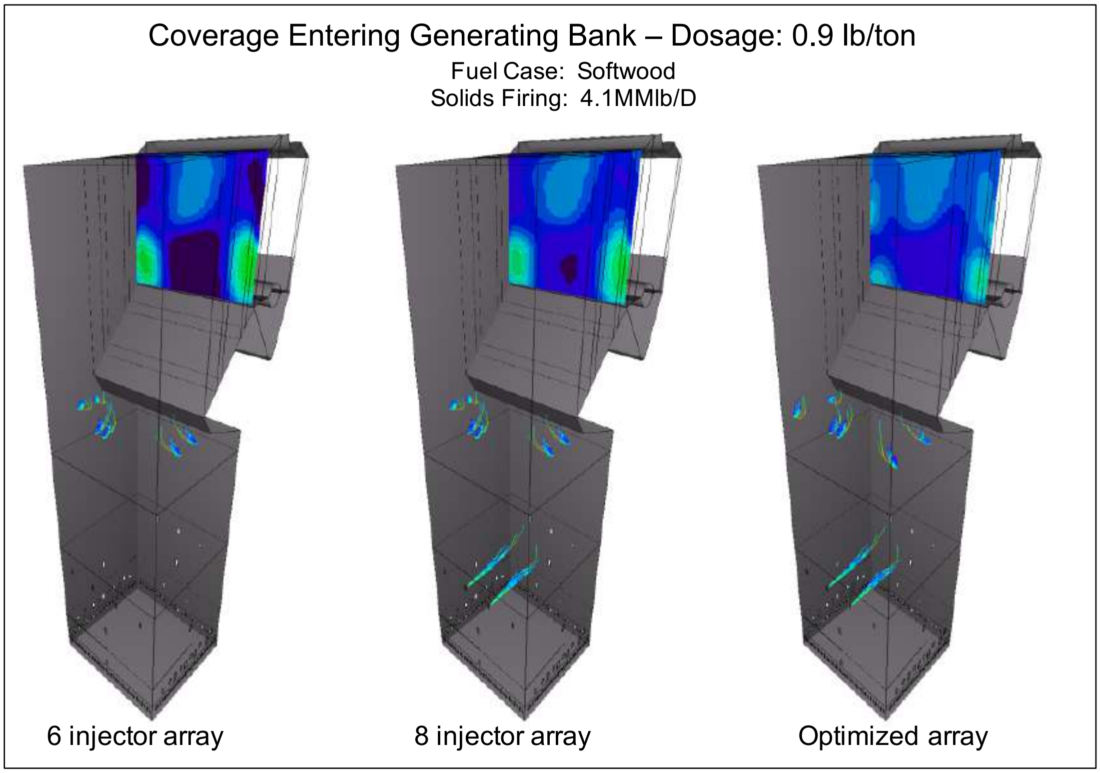


Figure 6. Optimization of Chemical Injection Strategy. Injectors are depicted as green cylinders, with colored streamlines. Colored streamlines depict calculated liquid droplet lifetimes prior to complete evaporation. Chemical distribution is represented at the generating bank with a colored contour map. Cold colors (purple and blue) denote low relative chemical concentrations, warm colors denote high relative chemical concentrations. Distribution is judged to be ideal when the contour map approaches uniform blue colors.

Proper selection of injectors is another key to successful targeting of problem areas. Chemical injectors are designed to atomize droplets into a fine mist so that during injection droplets rapidly evaporate. As described above, upon completion of droplet evaporation, $Mg(OH)_2$ particles flash calcine and rupture into numerous sub-micron-sized particles. Figure 7 illustrates one of approximately twelve proprietary injector types that this program can utilize to target chemical to problem areas. This particular injector atomizes droplets with compressed air, and the droplets form an extremely fine mist, resulting in droplet evaporation that occurs within inches from the injector tip.

Figure 7. Air-atomized chemical injectors selected to produce droplet size distributions that rapidly evaporate water droplets, while delivering chemical to problem areas. Note the fine mist and absence of large, falling droplets.

Once an effective injection strategy and appropriate injectors are selected, the system is installed in the recovery boiler. Following installation, the system is fine-tuned to optimize the cost-performance of the technology (see discussion below). Data from the unit is used to monitor performance, including: pressure differentials across heat transfer surfaces, attemperation spray flows, gas temperatures at various locations, heat flux sensors, and any additional signals that indicate the status of deposition. This overall methodology has been employed for over twenty years to monitor and optimize chemical additive feed rates and performance on over 100 combustion units of various types. Below is a detailed description of the system layout, baseline deposition and performance with chemical additive injection in a black liquor recovery unit.

Chemical Additive Performance Results (1995 – 2015)

Equipment

The equipment scope and layout varies from system to system, depending on the extent of deposition, size of the furnace, and degree of automation desired. A central tank is used to store chemical, and often a recirculation loop is used to continuously recirculate chemical to prevent slurry settling. The program is pumped and metered from the storage tank using several skid-mounted pumps. Chemical is pumped to mixing manifolds, mixed with dilution water, and pumped to injectors. A typical recovery unit will have several injectors (typically between six and twelve, depending on size and geometry) installed in various locations throughout the radiant section. Injectors are grouped and attached to a chemical mixing manifold that is outfitted with individual controls and gauges, allowing spatial control of chemical injection (*i.e.* flow biasing). There are also chemical injection pumps, water boost pumps and associated safety interlocks to permit flexibility to respond to major changes, if necessary. In this particular recovery boiler, a total of six injectors were historically used. Chemical consumption was monitored using a tank level indicator. Pumping and metering equipment is normally mounted on a skid.

Baseline Data

Prior to 1994, the pulp and paper mill had production runs limited to approximately 90 to 110 days before the recovery unit sufficiently plugged and had to shut down for water washing. As the recovery operation was tasked with increasing throughput from 2.4 million tons/day to 3.1 million tons/day of dry solids, carryover and fuming rates increased significantly. Sootblowing was the primary means used to control deposit build up; however, sootblowers lost their effectiveness as deposits grew, sintered, and hardened. Thermal shed procedures (*i.e.* "chill and blows") were effective immediately following shutdowns while the boiler was still relatively clean, but lost their effectiveness as the campaign progressed.

During baseline, (normal operation, no treatment) the differential pressure across the generating bank increased from 0.10 inches of water to 0.35+ inches of water gauge, at which point the unit would have to shut down for cleaning (Figure 8). To slow the rate of increasing *d*P due to slagging, the plant performed chill and blows (bringing the boiler down quickly from high load to low load and then ramping back up) at regular intervals in an attempt to clean the superheater and generating bank tubes. Each 90-110 days, the plant would shutdown and perform a water wash to clean tube surfaces.

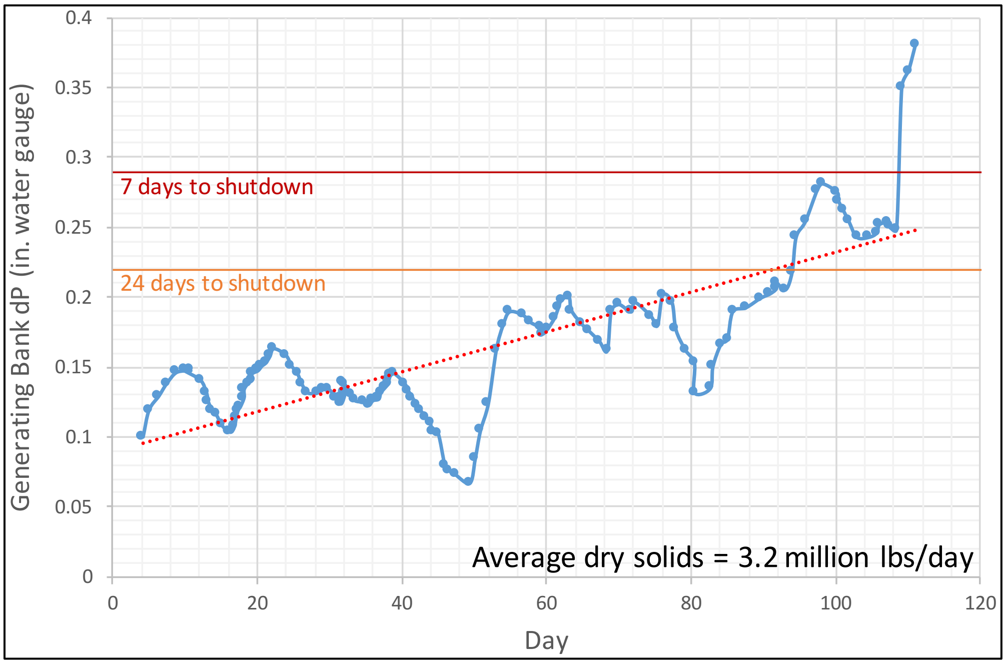


Figure 8. Generating Bank Differential Pressure During Baseline Run (1995). Mechanical and operational modification resulted in increasing throughput from a design of 2.4 million lbs/day of black liquor solids to 3.2 million lbs/day. The recovery boiler was able to operate for a maximum of 90-110 days between water washes. The horizontal lines on the graph represent the 0.22 inches of water threshold, when shut down was expected in 24 days and 0.29 inches of water gauge, the threshold when shut down can be expected in 7 days.

In an effort to increase run time between water washes, the mill evaluated a dry chemical additive program. The dry powder was blown in through tertiary air ports during this period, and little effect on furnace pluggage was observed, due in part to inconsistent feed of the additive. During the dry powder demonstration period, average daily dry solids throughput for this run was 3.2 million pounds. Least squares linear regression analysis indicated that deposition continued at a rate that was very similar to baseline (untreated), and resulted in a shutdown at approximately 110 days, when generating bank pressure differential approached 0.35 inches of water gauge. As such, no quantifiable improvement was observed with the dry chemical additive.

Generating Bank Differential Pressure with Program Injection

After conducting the combustion unit survey and identifying the problem areas within the recovery unit, CFD modeling was conducted and optimum injector locations were determined, as described above. Figure 9 illustrates the generating bank dP as a function of chemical additive injection. Initially, four injectors were placed into service 30 days into the first run. Two additional injectors were added on Day 37, upon optimization of the CFD model. With $Mg(OH)_2$ slurry injection into the recovery unit at a rate of 1.5 lbs/ton of dry solids, the unit remained below the maximum permissible generating bank pressure differential of 0.4 inches of water gauge. From days 0 through day 36 chemical was not injected and the generating bank dP approached 0.22 inches of water, the point at which shutdown is estimated in 24 days, based on historical data. Once chemical injection was initiated and optimized on day 37, the slope of the generating bank dP decreased and the unit completed the scheduled 97 day campaign without problem.

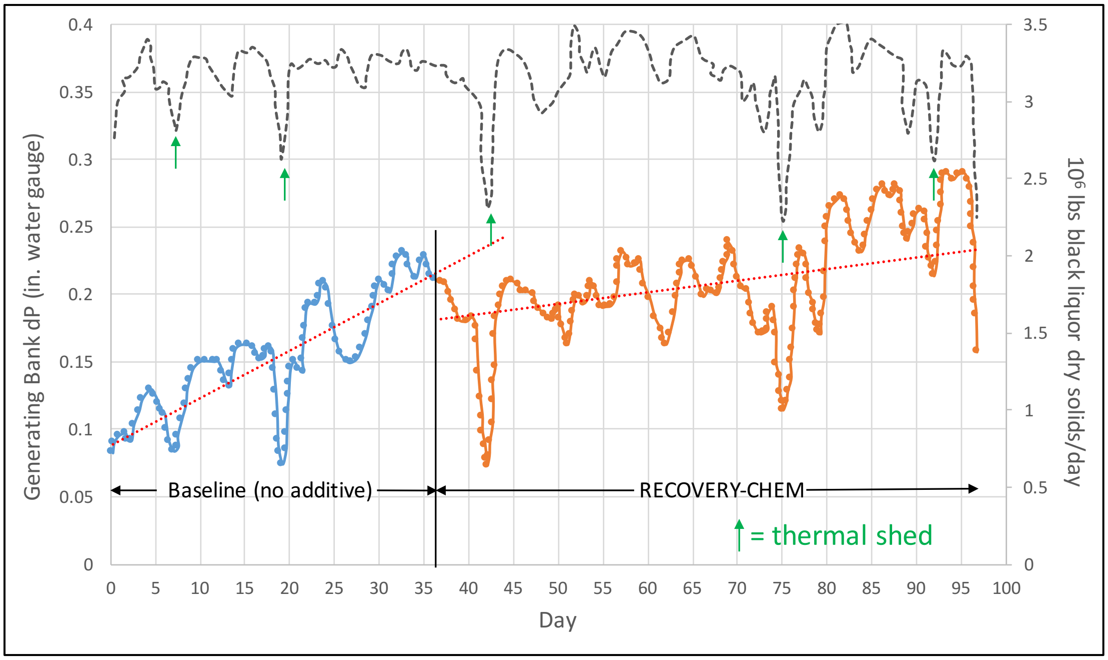


Figure 9. Generating Bank Differential Pressures During a 96-Day Campaign. The mill planned a 96-day campaign and attempted to achieve the goal without the use of chemical additive. Without the chemical technology, the generating bank dP increased rapidly and nearly resulted in a premature shutdown. After 37 days, the recovery boiler operators turned on the chemical program in an effort to extend campaign life to achieve the 97 day target. Injection of chemical additive technology at 1.5 lbs/ton of dry solids allowed the kraft recovery unit to achieve their 96 day goal. Additionally, with the chemical program, the frequency of thermal sheds (*i.e.* “chill and blows”) were decreased by 75%. Green arrows indicate thermal sheds.

In another campaign (Figure 10), $Mg(OH)_2$ injection allowed the recovery unit to run for the scheduled campaign run of 156 days. Proper application of chemical additive resulted in significantly more effective thermal sheds, keeping heat transfer surfaces clean, as observed during the previous campaign. Prior to program injection, thermal sheds were effective following water washing, when the boiler was clean, but thermal sheds decreased in effectiveness rapidly as the boiler fouled. With chemical injection, thermal shed procedures were decreased by 75% and each one retained effectiveness longer and maintained clean heat transfer surfaces. After 156 days, the unit was brought down in a plant wide shut down to install a new wastewater treatment facility, not due to excessive fouling.

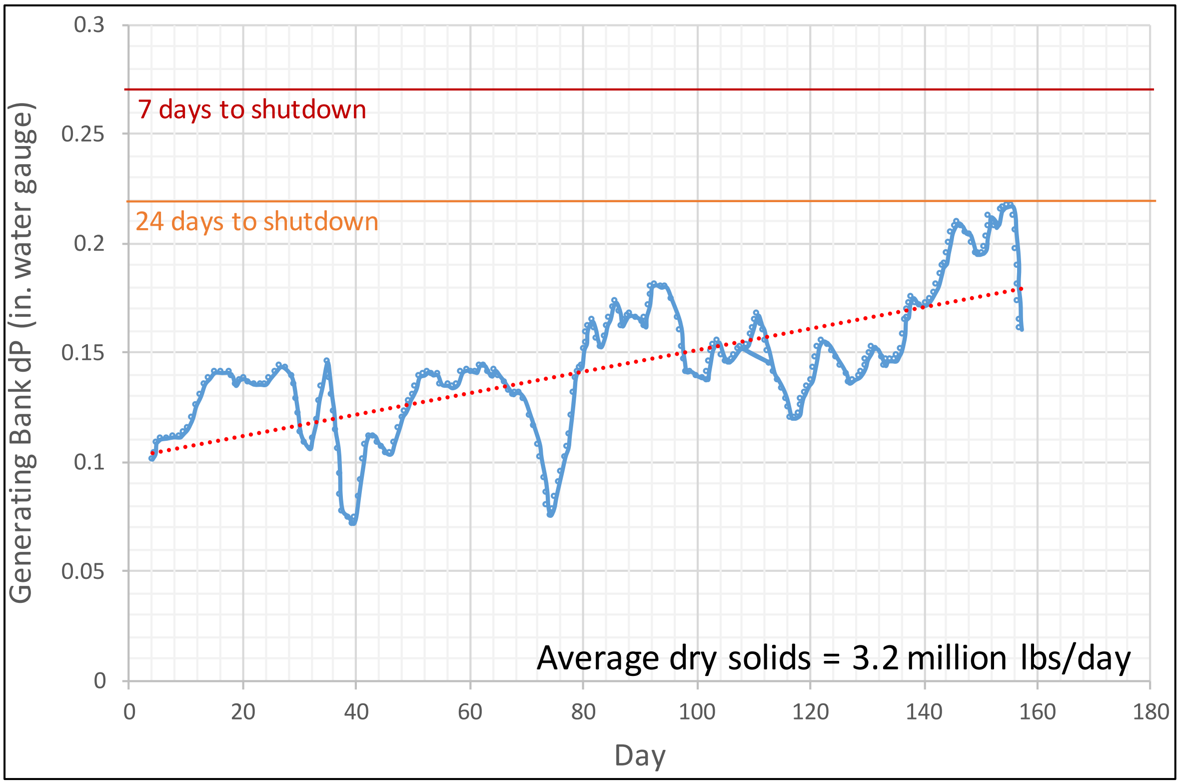


Figure 10. Generating Bank Differential Pressure with Program Injection. Targeted chemical injection resulted in decreasing the rate of pressure differential rise, allowing the mill to increase campaign life from a historical average of 90 days to the mill's stated goal of 130-160 days. Generating bank differential pressures were controlled by efficient sootblowing and occasional "chill and blows" (on days 38 and 73) with the aid of the $Mg(OH)_2$ slurry injection.

Dosage Optimization Trials

Dosage optimization trials were conducted after several years of the chemical injection system being installed on the recovery unit and numerous mechanical changes were made to the recovery boiler. Figure 11 illustrates the results of a dosage reduction trial completed in November and December of 1998. Prior to this trial several mechanical modifications were made to the recovery boiler, including: optimization of air distribution in the lower furnace, work was completed on the steam system to allow for higher steaming rates, and an SO_2 analyzer was put in place to aid in operation of the boiler.

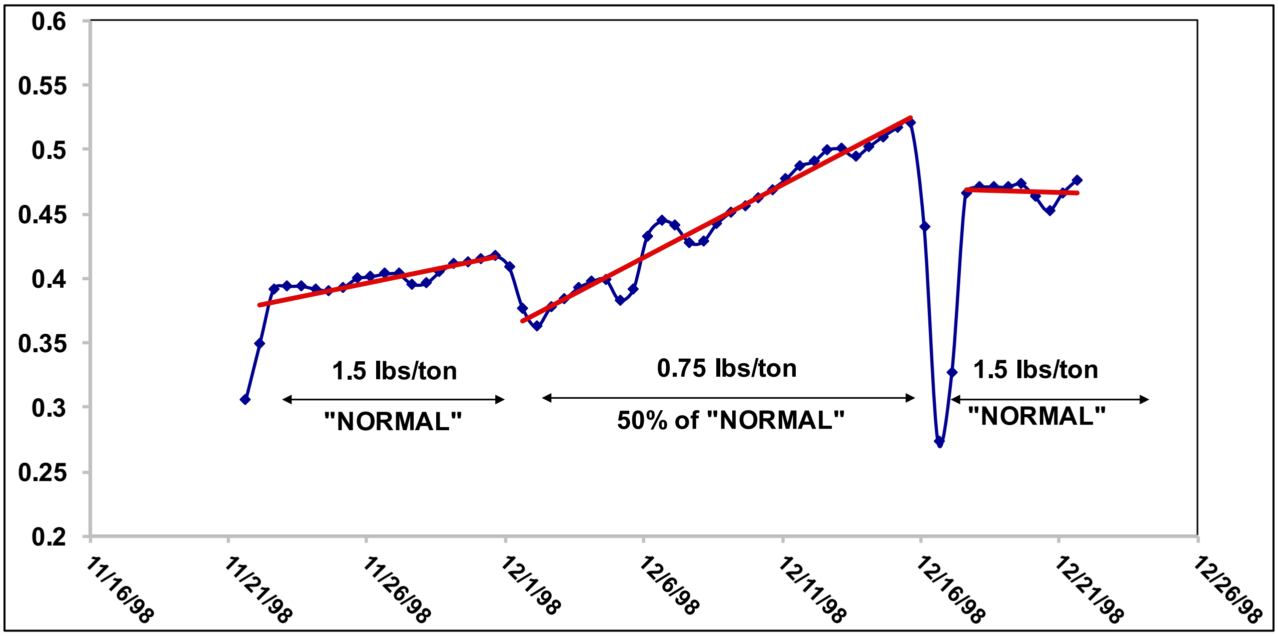


Figure 11. Impact of Chemical Additive Dosage Reduction on Generating Bank dP. Between 1995 and 1998, numerous mechanical and operational changes were made to the recovery unit. As such, in 1998, chemical dosage optimization trials were conducted to determine the most cost effective chemical dose necessary to meet operational objectives. In 1995, the optimal dosage was determined to be 0.7 kg/ton (1.5 lbs/ton). This dosage is designated as "normal". Generating bank differential pressure is denoted in inches of water.

During this trial the reagent dosage was reduced from a "normal" dosage of 1.5 lbs/dry ton solids fired to "50% of normal" dose of 0.75 lbs/dry ton of solids fired. Figure 11 illustrates the daily averages of the generating bank differential pressure as well as the corresponding least squares linear regression analysis of the periods of "normal" and reduced dosages. At the "normal" dosage of 1.5 lbs/ton of dry solids, the slope of the dP across the generating bank was relatively flat. When the dosage was decreased to 0.75 lbs/ton, the slope of the dP curve significantly increased. As such, the dosage was returned to and maintained at the "normal" level of 1.5 lbs/ton.

In 2000 the recovery unit operators began to partially purge the precipitator hoppers to reduce chloride buildup in the recovery unit in attempt to decrease corrosion rates. During this time, the operators conducted another dosage reduction trial, in an attempt to enhance the chemical additive program's cost effectiveness as a result of reduced chloride concentration in the unit. Figure 12 illustrates the impacts of dosage reduction on generating bank differential pressures. In the 1998 dosage reduction trial, the dosage was decreased from 1.5 lbs/ton ("normal") to 0.75 lbs/ton. In the 2000 dosage reduction trial, dosage reductions were made in smaller increments, specifically 10% below "normal" and 25% below "normal". The initial dosage reduction (10 % below "normal") began on August 16th. On October 3rd, the chemical additive dosage was reduced further to 25% below “normal”. In both cases, the slope of the dP curve across the generating bank increased from the “normal” injection rate condition, ultimately resulting in the need to clean the unit sooner.

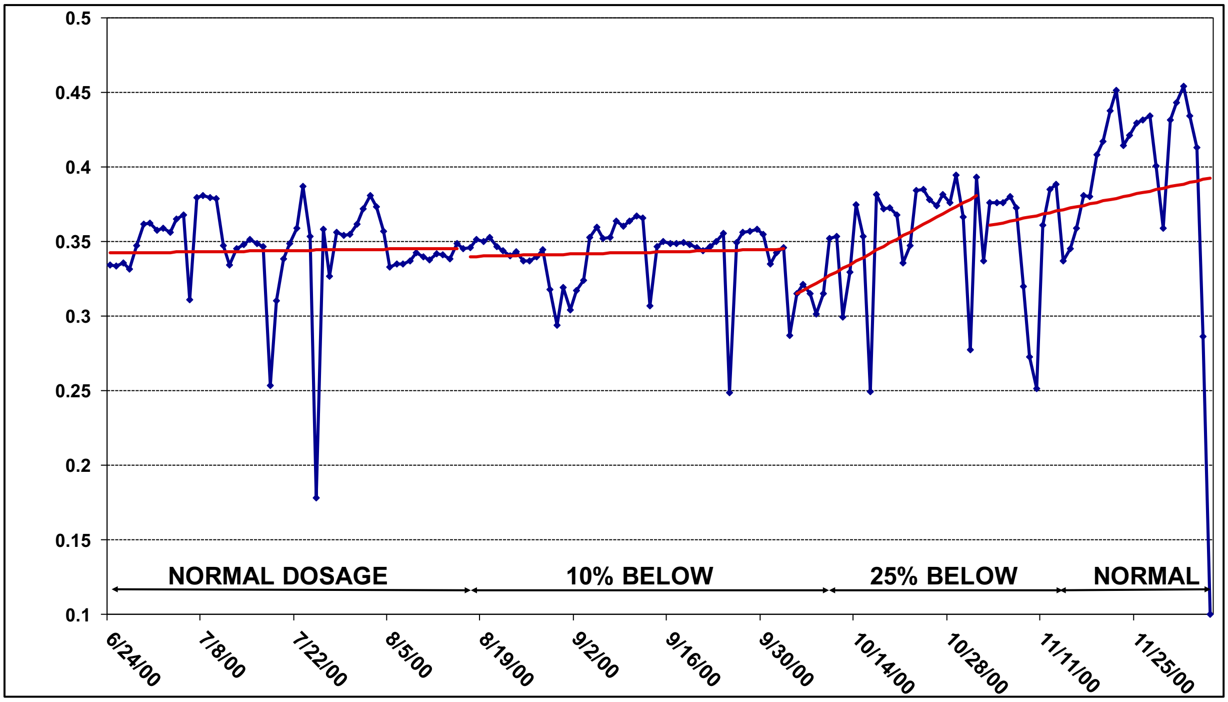


Figure 12. Impact of Chemical Additive Dosage Reduction on Generating Bank dP. In 2000, the chemical dosage was decreased by 10% and 25% and generating bank differential pressures were monitored to determine the optimal chemical dosage. The “normal” dosage is 1.5 lbs/ton. Generating bank differential pressure is denoted in inches of water gauge.

After the year 2000, the mill was processing fiber from a greater variety of wood species than in previous years. Specifically, the mill began to process northern softwood, hardwood maple, and hardwood birch. Initially, recovery unit operators were careful to store and process fiber by individual species to better understand the different firing methods required to reduce fouling with each wood species. At that time, the operators noted that hardwood species tended to foul the unit at much greater rates than softwood. As a result, in 2001 a dosage increase trial was conducted to evaluate the dosage required to prevent pluggage during campaigns in which hardwood was the primary wood species. To this end, the reagent feed rate was doubled to 3.0 lbs/ton of dry solids as fired during a period while the unit was on softwood to evaluate the impact of dosage increase under controlled conditions. However, the primary concern was for the upcoming hardwood run. By this time, campaigns were being conducted at an average 3.7 million pounds of dry solids throughput daily, a 54% percent increase over the designed throughput.

During the dosage increase trial, as dosage was increased from 1.5 lbs/ton ("normal") to 3 lbs/ton, the slope of the differential pressure curve was reduced from a positive slope to a negative slope during the short 30 day evaluation period. This run demonstrated that previously formed deposits were mitigated with the increased dosages by rendering sootblowing more effective. The campaign length goal of 120 days was met. During the outage the unit was thoroughly inspected, and operators indicated that at elevated dosages the unit was much cleaner than anticipated.

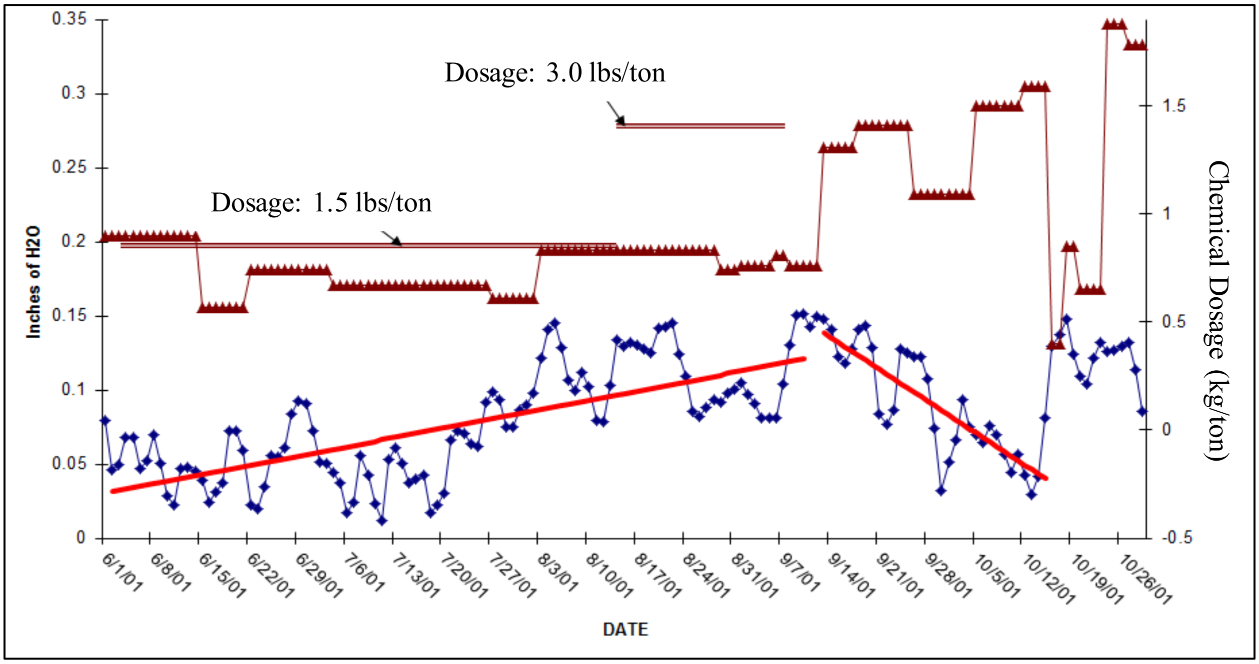


Figure 13. Dosage optimization trials at increased black liquor solids throughput at 3.7 million lbs/day. The as-designed black liquor throughput increased from 2.4 million lbs/day to 3.17 million lbs/day in the late 1990s. In 2001, the mill had a goal of increasing throughput to 3.7 million lbs/day. At a dosage of 1.5 lbs of additive/ton of dry solids, a campaign of 120 days was possible; however, increasing the dose to 3.0 lbs/ton reversed the rising differential pressure across the generating bank, permitting a six month run.

Since 2001, through a variety of additional mechanical and operational upgrades (*e.g.* ID fan upgrade, etc.), the unit increased throughput beyond 3.7 million lbs/day to 4.1 million lbs/day of dry solids (from an originally designed 2.4 million lbs/day). The combination of mechanical/operational upgrades and $Mg(OH)_2$ slurry injection has allowed the mill to extend campaign length beyond 3-4 months. In 2014-2015, a 320 day campaign was successfully achieved (Figure 14), the longest in mill history.

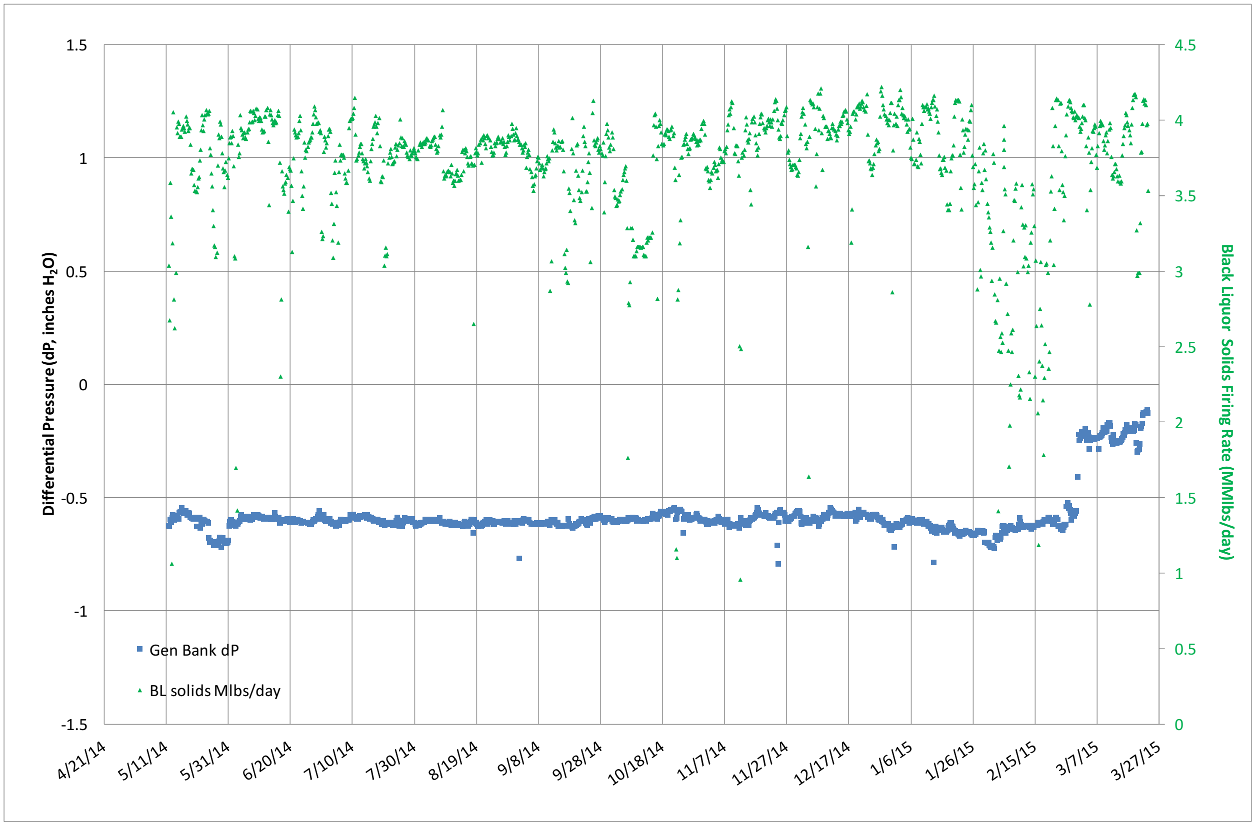


Figure 14. Generating Bank dP During an Eleven Month Campaign. Dry solids throughput averaged 4.1 million lbs/day. Chemical injection rates averaged approximately 1 lb/ton of dry solids. The sharp upturn in dP on February 1st is attributed to a fault in the generating bank pressure transducer.

After the eleven-month campaign in 2014-2015, an inspection of the unit revealed deposits above the nose, at the center portion of the inlet to the generating bank. Since achieving an eleven-month campaign, recovery unit personnel have indicated a desire to further increase campaign length to 18 months. Additional CFD modeling indicates that the addition of two injectors through tertiary air ports (with equivalent chemical dosage) will result in better chemical distribution at center portion of the inlet to the generating bank (Figure 6, right panel) and may afford campaign lengths to increase to 18 months.

SUMMARY

Deposits in black liquor recovery boilers can create significant production problems for operators and can result in decreased throughput, premature shutdowns, and safety concerns. Over the past several decades many mills have experimented with the use of chemical additives for deposit control with often inconclusive results. Through proper selection of chemistry, and targeted application, chemical additives can be used to control deposit formation. The targeted injection of magnesium hydroxide slurry has been demonstrated to be successful in rendering sootblowers more effective in deposit removal. A combination of CFD modeling, proper injector selection, and use of $Mg(OH)_2$ with advantageous physical properties has resulted in successful treatment of black liquor recovery boilers (as well as fossil fuel-fired boilers) for over twenty years. Proper chemical additive application can facilitate increased black liquor throughput and longer campaigns. As an example, through a combination of mechanical, operational, and targeted $Mg(OH)_2$ slurry injection, dry solids throughput at a North American mill was increased from an as-designed 2.4 million lbs/day of dry solids to 4.1 million lbs/day of dry solids, and campaigns increased in length from a maximum of 90 days to 11 months.

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