The realization that chlorine-based pulp bleaching sequences exhibited a significant and potentially negative impact on the environment, and the promulgation of the “Cluster Rules” [1] in the United States and similar regulations in several other countries [2-6], led to a virtual explosion of research examining alternative bleaching chemistries during the late 1980s and early 1990s. Several alternative chemicals were investigated, including, but not limited to, peroxide [7], peroxyacetic acid [8], peroxyformic acid [8], potassium peroxymonosulfate (Oxone) [8], dimethyldioxirane [9] (which is generated in situ from acetone and potassium peroxymonosulfate [9]), peroxymono-phosphoric acid [10], various enzymes [11,12], polyoxomolybdates [13], Monox-L [14,15], dithionite [16], ozone [17-21], chlorine dioxide [22-24], and oxygen [25,26].

Research into the formation of adsorbable organic halogens (AOX), chloroform, and other bleach plant pollutants showed that higher kappa number pulps entering the bleach plant tended to increase the amount of these pollutants being formed [27-29]. As a result of these findings, a significant amount of research effort was expended on developing methods that could be used to reduce the kappa number of pulp entering the bleach plant. Some of these efforts included cooking modifications to extend delignification in the digesters [30-34]. Other methods of lowering the entering kappa number included the use of oxygen bleaching [35,36] and enhancements to oxygen delignification, including pretreatment with nitrogen dioxide (Prenox) [37], and the use of nitrosylsulfuric acid (NSA) [38].

By the end of the 1990s, commercial bleaching sequences had evolved to virtually eliminate chlorine and hypochlorite as viable bleaching chemistries [22]. Most of the kraft pulp industry had settled on elemental chlorine free (ECF) bleaching as the sequence of choice. ECF bleaching sequences tend to use chlorine dioxide, caustic, oxygen, and peroxide as the main bleaching chemistries [39,40].

As individual mills examined alternatives to address the environmental drivers, additional factors influenced strategies for modifying pulp bleaching sequences. Better control of production costs and process efficiency, attainment of evolving product quality specifications, and minimization of effluent volume and air emissions were the result. Not surprisingly, the mix of these pressures, in conjunction with a host
of site-specific considerations (plant size, location, existing equipment, water availability, receiving stream characteristics, etc.), has yielded mill-specific strategies for achieving a mill’s specific bleaching objectives [41].

One aspect that weighed heavily on the determination to use ECF bleaching techniques was the cost of bleaching chemicals and/or new equipment [42]. Several of the exotic bleaching sequences resulted in bleaching costs of upwards of $100 per ton. The digester and prebleaching methods for reducing the kappa number of the pulp required substantial capital for limited or no payback. As a result, mills became extremely conscious of the fact that bleaching costs and bleach plant operation were critical to the profitability of the mill [43].

Because of the extensive cost associated with ECF conversion and the volume of alternate bleaching chemicals that were investigated, and because the excitement that characterized the 1990s about totally chlorine free (TCF) bleaching, with its panoply of esoteric chemicals and exotic bleaching sequences, had ended, the quantity and direction of bleaching research changed. Since that time, significantly less research effort has been expended on fundamental development of new bleaching chemistries. Rather, research and development efforts have focused on addressing the various problems of the existing ECF operations and developing solutions for immediate implementation [43].

**MODELING APPROACHES TOWARD OPTIMIZATION OF ECF BLEACHING SEQUENCES**

Once the ECF option was established as the dominant bleaching sequence for kraft pulps, much research focused on determining the fundamental operations of individual bleaching stages [44-51]. Efforts to optimize each bleaching stage in isolation have often resulted in overall sequence sub-optimization. Changes made to one stage in a sequence inevitably affect the operations of preceding and subsequent stages. Additionally, a large number of parameters need to be determined, tuned, and validated experimentally to successfully simulate the dynamic nature of bleach towers [45,52-59]. The non-linear nature of first principle bleach plant models can make computational optimization difficult to perform.

Another type of model that has been used for optimization is the neural network approach. These types of models typically are used as a “black box” within a process control system. Statistical relationships are used to determine the relationship between dependent and independent variables, which are then connected with heuristic algorithms designed to obtain specific operational objectives. Neural network systems are based on operating mill data, and therefore are relatively insensitive to process noise [60]. One negative aspect of neural network systems is that the predictive capabilities of these models are limited to the range of the operational data from which they are developed. Often, the operational ranges of input variables are narrow and the optimum conditions may lie beyond these ranges, thus limiting the usefulness of these models [61].

More recently, efforts have been made to model and understand how best to optimize the overall ECF sequence from a holistic and economic approach. These models have used steady state bleach plant balances to optimize the process; process dynamics are ignored. Frequently, mill specific economic data are combined with the models to determine optimal economic conditions for a specific set of operating conditions.

**STEADY STATE MODELS**

Early steady state models typically broke the bleach plant into delignification stages [52,62] or brightening stages [46] and restricted model optimization to those segments of the bleach plant. Researchers have successfully integrated the two portions of bleach plant operation (delignification and brightening) into consolidated models covering the entire bleach plant [63-69]. Many of these models have focused on minimizing chemical usage or cost at a given brightness for a specific incoming brownstock pulp. These models typically are predicated on stoichiometric relationships of kappa number reduction or brightness gain for a given amount of bleaching chemical used.

In spite of substantial progress in developing steady state models for ECF-based bleach sequences, some constraints remain in using these models in actual mill applications. One such constraint is the inability of these models to handle variable brownstock or oxygen delignified pulps and variable kappa number pulps coming into the bleach plant. This issue limits the usefulness of a steady-state bleach sequence model if it is coupled with other steady state models for unit operations, such as the digesters, washers, and recovery, for overall pulp mill optimization. Recent steady state model efforts have successfully overcome this limitation and show the utility of steady-state bleach sequence models, which can vary the incoming softwood pulp kappa number into the bleach plant when coupled with variable incoming kappa number pulps [63,70]. Other researchers have successfully modified the delignification stoichiometric models to incorporate the effect of oxygen reinforced extraction into more universal modeling efforts [54,71].

**DEVELOPMENT OF A STEADY STATE MODEL**

A steady state model can be created in several different ways. Detailed descriptions of several types of models and their development are available elsewhere [72]. For this review, two distinct types of model development will be considered: the stage-wise integration of several different models [63,70] and the use of a process simulation program such as WinGEMS (Metso; Helsinki, Finland) as the basis for steady state model development [58,59,70,73,74]. Both types of model development require a substantial amount of data to accurately model a bleach plant. Both laboratory data and mill process data may be used successfully in model development. In many cases, combinations of mill and laboratory data are used to develop the models. In some instances, literature data may be obtained to supplement existing operational or laboratory data [73].
Typical examples of laboratory and mill data used in the development of two distinct steady state model studies [63,70] are described in this section.

One study prepared laboratory pulps and bleached the resulting pulps [63]. The laboratory data and methods used to obtain these data included the pulping of southern softwood furnish in a laboratory digester designed to simulate extended modified continuous cooking (EMCC) kraft pulping. The temperatures and effective alkali parameters were adjusted to achieve a series of eight pulp furnish with kappa numbers between 13 and 34. Total and screened yields were measured on each cook. After these pulps were well washed and screened, they were subjected to treatment with xylanase enzymes and bleached.

In another study [70], laboratory and mill operational data were combined to develop the working models for the effort. Pulp yield and black liquor properties were obtained from laboratory cooks at various kappa numbers performed with mill chips and mill liquors in a laboratory digester. Tests of sodium carryover to the bleach plant were performed with an inductively coupled plasma (ICP) analysis on squeezed liquor samples and on nitric acid solubilized pulp obtained from an operating mill. The effect of brownstock washing carryover on acid and bleach plant chemical demand was determined by spiking an extremely well-washed mill pulp with various levels of final stage washer effluent and performing laboratory bleaching to a constant brightness. Several of the evaluated conditions (kappa number 20, 26, and 28) were performed with data collected from an operating mill. Mill data were also obtained from washing studies performed at 3.0 and 3.5 dilution factors.

For the digester operation portion of this work, mill data were collected for two sequential 11-week operating periods. During the first 11 weeks, the digester was being operated in downflow conditions. EMCC operating conditions were used during the second 11 week period [70].

These laboratory and mill data were used to tune various process models to cover the entire operating ranges evaluated. Steady state process models were developed with WinGEMS models tuned with the mill and laboratory data. Base case chemical costs were arbitrarily chosen to be relatively representative of actual costs within a generic pulp mill operating during the 2005-2007 timeframe. No actual mill costs were obtained for this work [70].

After sufficient data are obtained, process simulation models can be pieced together to represent either an operational or virtual bleach plant, or different models can be combined to represent the entire process. An example of using multipurpose process models to develop a complete bleach plant simulation might include using work reported by McDonough [46], which has shown that $D_1$ or $D_2$ brightening responds to chlorine dioxide ($ClO_2$) charge by the following equation:

$$y = b_0 + bg(1-\exp[\frac{x}{r}])$$  \hspace{1cm} (1)

In this equation, $y$ is the brightness and $x$ the $ClO_2$ charge. Because of the nature of the equation, the term $b_0$ is the initial brightness before $ClO_2$ addition. The term $bg$ represents the maximum achievable brightness for the $D$ stage under the specific conditions of the simulation. The maximum brightness is typically referred to as the “brightness ceiling.” The term $r$ describes the rate at which the brightness ceiling is approached. It is equal to the amount of $ClO_2$ at which 62% of the brightness gain is achieved.

This curve is reported [63] to provide a good fit for the $D_1$ or $D_2$ stages, and for the DE kappa response to $D_0$ $ClO_2$ charge. Note that the DE kappa is the kappa number of the pulp mea-

![Graph](image-url)

1. EP kappa versus $D_0$ $ClO_2$ charge [63].
sured at the end of the first caustic extraction stage.

\[ y = k_0 - k_d (1 - \exp \left[ \frac{x}{r} \right]) \]  

Again, \( x \) is the \( \text{ClO}_2 \) charge, \( y \) is the DE kappa at constant E stage conditions, \( k_0 \) can be approximated by the initial brownstock kappa, and \( k_d \) becomes the maximum change in kappa between the brownstock and the DE pulp at constant E stage conditions. The concept of brightness ceiling is exchanged for “kappa floor,” the DE kappa beyond which no amount of \( \text{ClO}_2 \) will yield a lower kappa.

Using the previous equations, the DE kappa response can be determined for each pulp involved in the study. The relationship between the parameters (\( k_d, r \)) and brownstock kappa is nearly linear over the range of kappa numbers typically evaluated by model studies. For modeling purposes, the entire data set is regressed to determine the form of the following equations:

\[ y = k_0 - k_d (1 - \exp \left[ \frac{x}{r} \right]) \]  
\[ k_d = a + b \cdot k_0 \]  
\[ r = c + d \cdot k_0 \]  

After the constants, \( (a, b, c, \text{and } d) \) are known, \( y \) may be solved for any given \( k_0 \) and \( x \). **Figure 1** shows an example of this approach, where the calculated curves are fit to the experimental data [63]. **Figure 2** shows a contour graph of the model.

The 28 different brightness and kappa D(EP) pulps from a previous study [63] were each subjected to a series of two, three, or four \( D_1 \) \( \text{ClO}_2 \) charges to determine the brightness response curve from Eq. (1). The parameters \( b_g \) and \( r \) were correlated to the initial brightness via linear regression. The result is a model that predicts brightness based on initial brightness and chemical charge based on the following equations, where \( b_g = a + b \cdot b_0 \) and \( r = c + d \cdot b_0 \):

\[ y = b_g + b \cdot \left(1 - \exp \left[ \frac{x}{r} \right] \right) \]  
\[ k_d = a + b \cdot k_0 \]  
\[ r = c + d \cdot k_0 \]  

The series of graphs in **Fig. 3** show that the equations provide a good fit to the previously reported data [65]. The series of graphs were fitted for pulp C at 0.15, 0.25, and 0.45 kappa factor (upper left corner of figure), for pulp D at 0.10, 0.25, and 0.40 kappa factors (upper right corner of figure), pulp H at 0.10, 0.20, and 0.40 kappa factors (lower left corner of figure), and for pulp F at 0.15 and 0.35 kappa factors (lower left corner of figure). Excellent agreement was obtained between the experimental data and the best fit curves. **Figure 4** shows the contour graph of the full model.

Because the EP stage in the laboratory simulation was operated at a constant peroxide charge, a constant relationship is assumed to exist between the EP stage kappa and brightness. **Figure 5** shows this relationship, which can be used to provide the link between the \( D_0 \) (EP) model that predicts kappa and the \( D_1 \) model that requires EP brightness as a variable. It may be possible to replace this assumption with recent work that has successfully incorporated the effect of oxidative reinforcement in the extraction stage into unified models for hardwood [71] and softwood [64] bleaching. A linear equation describes this curve:

\[ y = a + b \cdot x + b/x \]

where \( y \) represents brightness and \( x \) represents the EP stage kappa.

The final P stage was modeled with laboratory data from a previous study and fitted with an equation similar to Eq. (2). With these four equations, the entire D(EP)DP bleaching response to chemical charges and entering brownstock kappa number may be modeled with a spreadsheet.
3. Brightness response to ClO$_2$ charge [63].

4. D$_1$ stage model [63].
USING PROCESS SIMULATION PROGRAMS

Another way to develop steady-state bleach plant models is to use commercially available process simulation programs such as WinGEMS. The initial development of a WinGEMS program can be as simple as putting together a series of unit operations and connecting pipes into a flow sheet represented by blocks and lines. The user can specify the number and type of major components within a specific stream. Water, fiber (or total suspended solids), total dissolved solids, and temperature may be sufficient for simple material and energy balances. For more complex simulations, several additional components, such as bleaching chemicals, bleaching reaction products, and various ions may need to be specified.

Stream components represent materials and properties of materials used in the WinGEMS calculations. All stream components together define the composition of the stream. A single stream structure is set up for each simulation project [75]. Because of the complexity of the reactions involved in the bleaching process it is important to understand the degree of complexity required for a specific project. If equipment changes or modifications are sought to affect a relatively simple water balance change, to limit the number of stream components could be limited to simply water, temperature, suspended solids, and dissolved solids. If a more complex modeling task is being considered, such as predicting the effect of new equipment on the scaling or corrosion potential of the bleach plant, several reaction products and chemical concentrations would be included within the stream component system.

Specific unit operations are represented in WinGEMS by various calculation blocks. For example, washer blocks and separation blocks can be used to represent pulp washing devices and screens. The user can specify the efficiency of these types of blocks to represent physical inefficiencies found within operating systems. There are also dilution blocks that will use various inlet streams to dilute other streams to a representative consistency and reaction blocks that can convert one stream component into other stream components to represent chemical reactions. Often, however, WinGEMS does not have calculation blocks for special unit operations or blocks detailed enough for the user. In this case, the user can take a generic calculation block and adapt it for a specific unit operation. In some cases, several blocks might be required to represent a certain unit operation. In WinGEMS, control blocks can be used to attempt to force a specific stream to a specific value.

WinGEMS also has DDE (dynamic data exchange) which allows it to take or send data to an Excel spreadsheet. By tying the DDE into an equilibrium solver in Excel, WinGEMS has been successfully used to predict calcium oxalate and barium sulfate scale formation within a bleach plant [76,77].

Once a steady state model using individual stage performance equations is incorporated into a spreadsheet (described previously [63]), or of the process simulation type represented by WinGEMS [58,59,70,73,74] or MAPPS [78], or a simple spreadsheet model [79,80] has been prepared, it may be applied in several different ways. These types of models may be used to help design or justify capital expenditures within a mill’s bleaching process [70,73,76,79,81], used to minimize the application of a specific bleaching chemical...
[52,57,59,82], or used to minimize the total bleaching [52,54,56,57,61] or total pulp production costs [63,66-68,70]. Steady state models may also be used to help determine the impact of process changes on operational [76,77,80] or environmental performance [82].

**PROCESS OPTIMIZATION WITH STEADY STATE MODELS**

Simulations can be very detailed or very general depending on the end-use requirement. A very detailed simulation can help troubleshoot problems by finding bottlenecks in the system, can check the accuracy of measurement instruments, determine the potential for oxalate or barium scale, or can be used to optimize specific unit operations or the entire process. More generalized material and energy balance simulations are often used on a mill-wide basis to perform economic calculations when major capital projects are being considered and the benefits need to be estimated [83].

Steady state bleach plant models have been used successfully to minimize bleaching sequence costs by predicting chemical application tradeoffs in conjunction with relative costs for each of the bleaching chemicals. Even if the cost of the chemicals increased, it was not uncommon for the relative costs to remain fairly similar. As a result, many bleach plants have tended to operate with production targets that have either been set many years ago or have simply been developed as collective knowledge about how a specific mill runs best. Many of these targets (e.g., kappa number from the digester, amount of applied wash water, conductivity going into the bleach plant, and amount of bleaching chemical applied in various bleaching stages) directly impact the variable operating cost of the mill.

It is important to realize that a mill may easily sub-optimize one specific area of the mill without realizing the negative effects that sub-optimization has had on other operating areas of the mill. Typical examples of sub-optimization would be a mill endeavoring to minimize bleaching cost without accounting for the impact on woodyard or evaporator costs [63] or a mill attempting to increase pulp yield from the digester without determining the effect on power generation or bleach plant costs [73].

For several decades, these type of operating targets have served pulp mills reasonably well because chemical and energy costs tended to change slowly and relative to each other. A few years ago, the trend of slow and relative changes of chemical and energy costs was broken by a rapid escalation in energy costs [84]. In part as a result of rapidly escalating and volatile energy costs, many mills focused on millwide energy reduction projects during the mid-2000s [85,86].

Recently, chemical prices have also started to experience radical and erratic escalations. Prices for typically cheap commodity process chemicals have increased several fold. Sulfuric acid, for example, a traditional, long-term low cost commodity, has increased several hundred percent in price in association with its use in fertilizer production [87]. Caustic, another long-term, historically inexpensive process chemical, has increased in price by more than 100% as a result of an imbalance in chlorine-caustic demand resulting from the dramatic slowdown in new home construction [88]. Many other chemicals have also substantially increased in price as a result of changing demand and increased energy costs.

The net result of all of these changes has been a need to understand the trade-offs between different bleaching chemicals and how these chemicals may be applied to obtain a target brightness for a specific operational bleach plant. By performing several parametric studies with different amounts of applied bleaching chemicals in different stages, then applying actual chemical costs to each bleaching sequence, a minimum cost structure for a specific set of chemical and energy cost scenarios can be determined. This type of modeling approach has been used successfully for varying chemical and energy scenarios [63,70]. An example of this type of model optimiza-

![Graph](image)

6. Optimal kappa number target for increasing chemical and energy costs [70].
tion (Fig. 6) might be the determination of the optimal kappa number under variable chemical and energy scenarios [70].

Parametric studies can be used to develop a series of curves for different target outcomes and to develop optimal cost operating targets for specific mill operations. For example, when trying to minimize the total production cost, it is important to determine the best pulp brightness target and the optimal kappa number of the pulp entering the bleach plant. Wood costs can account for 60% of the total variable costs of producing pulp so yield plays an important role in the costs. As the kappa increases, the bleaching cost increases. However, wood costs decrease as a result of the kappa-yield relationship. With the aid of a steady state model it is possible to predict costs (wood plus bleaching chemicals) for various final brightness targets in the bleach plant. Figure 7 details these cost curves by showing the effect of digester kappa number as a function of total wood plus bleaching costs for various brightness targets leaving a specific bleach plant. At the 84%-88% ISO targets, the 34 kappa is the most optimal for cost. At the 89% ISO target, a 27 kappa is optimal, while the 90% ISO target gives an even lower optimum kappa at 21. The brightness ceiling affects the optimum cost to kappa number for a given fiber line.

7. Effect of brownstock kappa on relative total wood and chemical cost [63].

**USING EQUILIBRIUM-BASED MODELS FOR DESIGN OF CAPITAL PROJECTS**

In addition to optimizing chemical applications and minimizing pulp production costs, steady state bleach plant models have been successfully used to predict the impact of various capital investments on bleach plant operation [76,77,79,82,83,89-91]. Typically, multiple capital scenarios may be used to obtain a specific project goal. By modeling the performance of the different pieces of equipment, a mill may predict a priori the impact of various capital expenditures on the chemical addition, production cost and environmental performance of the mill. If a sufficiently detailed simulation is used, the mill might even be able to predict the impact of suggested operating conditions on oxalate [76,82,89] and barium [77] scaling potential and predict changes in operating conditions to minimize or eliminate scale before the improved bleach plant is even built [76].

Since the advent of ECF bleaching, several studies have been performed to predict the effect of replacing drum and diffusion bleach plant washers with wash presses [76,79,82,83,90]. Several of these studies have evaluated the ability of presses to reduce water emissions and have determined the effect of reduced chemical carryover between various bleaching stages on final chemical use in the modified bleaching process. In several instances, the predicted reduction in chemical charge has been used as part of the return justification required to obtain job approval.

Another area where process modeling has been extensively used is in the prediction of oxygen delignification performance on operating costs, recovery boiler operation, and pollution abatement [91]. Detailed modeling has been used successfully to show that oxygen delignification has some effect on bleaching cost and a small effect on recovery boiler operation. It also exhibits a fairly significant effect on environmental emissions from the bleach plant into the waste treatment plant, and a rather large capital expenditure.
CONCLUSIONS
Steady state bleach plant models ranging from simple spreadsheets to detailed process simulations using dynamic data exchange in conjunction with external equilibrium solvers have been successfully used to optimize chemical additions, bleaching chemical and total pulp production costs. These types of programs have been used to help predict the impact of process and capital changes to the bleach plant on operating costs and environmental parameters of importance to the mill and to governmental compliance agencies. These programs have also been used to optimize process operating conditions to predict and prevent oxalate and barium scale formation even before the bleach plant modifications have been approved for construction.

Several researchers have successfully modified and improved previous models to enhance the prediction capabilities of these process models. Good effort has been made on incorporating incoming brownstock kappa number, the use of oxidants in the extraction stage, and in understanding the impact of ClO₂ application in the last stages of the bleaching sequence.

In more recent years, with the relative costs of various bleaching chemicals and energy moving somewhat independently of each other, bleach plant models have been used to minimize the impact of spikes in chemical and energy costs. In most situations, simple parametric studies have been sufficient to determine optimal conditions. No sophisticated equation solver was required to determine operating conditions moving towards optimal solutions. With further advances in modeling and computing power, the speed of performing parametric studies has increased to the point that a well-trained process engineer could potentially enter daily performing parametric studies has increased to the point that a well-trained process engineer could potentially enter daily moving towards optimal solutions. With further advances in modeling and computing power, the speed of performing parametric studies has increased to the point that a well-trained process engineer could potentially enter daily parametric studies has increased to the point that a well-trained process engineer could potentially enter daily operating parameters such as brightness targets. TJ

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LITERATURE CITED
ECF BLEACHING

75. Metso Automation, WinGEMS Help: Stream Components Version 5.3 (Build 305), Metso Automation, Tampere, Finland, 2005.
Multiple articles have been published dealing with bleach plant optimization. Some of these articles attempted to use mechanical and chemical engineering principles to predict optimal performance of single bleaching stages and of unified bleaching sequences. Others have attempted to merge cost and operating data in either steady state or empirical models to predict cost optimization. This literature review attempted to pull several of these models into a single report to enable the reader to better understand the potential application of modeling in bleach plant optimization efforts.

Some of my previous research has developed steady state chemical and economic models to help determine optimal conditions for kraft pulp bleach plants. The current work combines my past work with the work of multiple other researchers to demonstrate the strength and weaknesses of various modeling approaches toward bleach plant optimization.

In compiling this review, I was impressed by the multitude of chemical and hydrodynamic bleach stage studies that have been performed in the last 20 years.

Hopefully, mills will be able to develop an improved understanding of the various bleach plant models that are available to them and determine the degree of complexity (or simplicity) that is truly required to optimize their own bleach plants.

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