Virtual Bleach Plants Part 1: Mill applications

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ABSTRACT: The "Virtual Bleach Plant" (VBP) is a new simulation approach that tries to "duplicate" real mill bleach plants in "one model". This model contains information for operations, environmental management, and capital investment. Users can selectively output simulation results for their own applications.

This paper is the first of a series in which subsequent papers describe predictive bleaching models and their applications to elemental and totally chlorine free (ECF and TCF) bleach plants. An overview of these later papers is included below.

In this paper, the VBP is applied to two mill bleach plants. Case A demonstrates the VBP's ability to duplicate real mill bleaching, comparing several VBP simulation results with mill measurements. In Case B, we use the VBP as a tool for mill bleach plant improvements. The simulation predicts the effects of shifting from 65% ClO_2 substitution to ECF and adding peroxide reinforcement in caustic extraction.

Application: VBP can help mills better evaluate economic, environmental, and product quality issues.

Process simulation has been widely used in design or research oriented work, such as evaluating new technologies in mill systems (1). The result of using process simulation to address industry concerns for pulp and paper is mixed. The main reason is that commercial process simulators for the pulp and paper industry, such as WinGEMS (2), mainly are mass and energy balance tools. Basic industry processes, such as cooking and bleaching, still do not have predictive models in these simulators. Therefore, these simulators are effective only for issues related to mass and energy balance calculations, such as determining bleach plant steam usage. Such simulators cannot choose the more economic process from two bleaching sequences because models in these simulators cannot predict all chemical consumptions and brightness. However, if suitable models are available, simulation can address complex mill issues. Recently, simulation was demonstrated as a practical tool for volatile organic compound (VOC) MACT compliance (3).

Although good bleaching models have not been available, useful information in the bleaching research literature is abundant. When literature information is consolidated into model format, the results from basic research can be used directly to address mill issues through simulation. In this series of papers, we make a step in this direction. Although the bleaching models in these papers are not perfect, they show promise for addressing mill bleaching issues. The case studies in this paper demonstrate how well these models match reality.

OVERVIEW

Although mass and energy balances for bleach plants have been routinely calculated in existing process simulators, there is a significant limitation. No predictive bleaching chemistry is included. Therefore, current simulators cannot address issues related to bleaching, such as the impact of chemical charges on brightness gains. The Virtual Bleach Plant (VBP) tries to remove this limitation. Furthermore, VBP simulation provides all information related to bleach plant operations (e.g. COD generation and scale prediction).

Virtual Bleach Plant concept

The Virtual Bleach Plant (VBP) is a set of simulation tools that aim to "duplicate" mill bleach plants in computer models. Conventional modeling only includes mass and energy balances. The VBP tries to provide all information related to bleaching fundamentals and bleach plant operations, including the following:

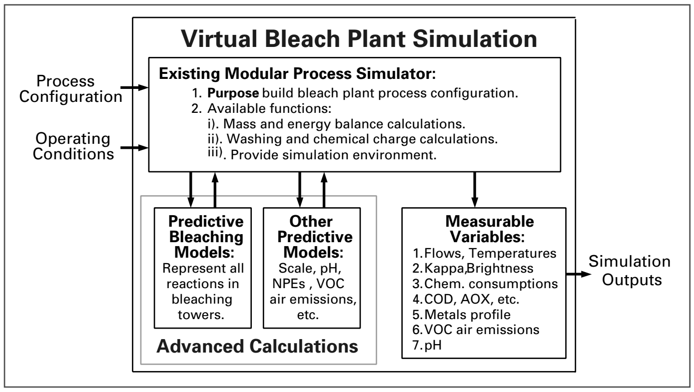
1. Process configuration, washing efficiency, etc. (conventional simulation from existing commercial software)
2. Delignification, brightness, yield and cleanliness calculations from predictive, kinetic, bleaching models
3. Detailed filtrate component predictions (Environmental parameters, such as COD and AOX, can be calculated from these filtrate components)
4. Scale prediction and other NPE distribution from metals equilibrium calculations
5. pH profile and caustic/acid consumption calculations from bleaching models and equilibrium calculations
6. Other advanced process calculations, such as VOC air emission prediction.

The most important component in the VBP is a set of predictive bleaching models. These new models represent all chemical reactions in bleaching and the effects of these chemical reactions on pulp properties and bleaching filtrates. These bleaching models are integrated into an existing process simulator that can represent mill process configuration and perform mass and energy balance calculations. Therefore, in VBP simulation, bleaching chemical calculations are performed under the operating conditions and process interactions of the simulated bleach plant. The real mill bleach plant is thus "duplicated" in simulation and the behavior of the actual bleach plant can be analyzed.

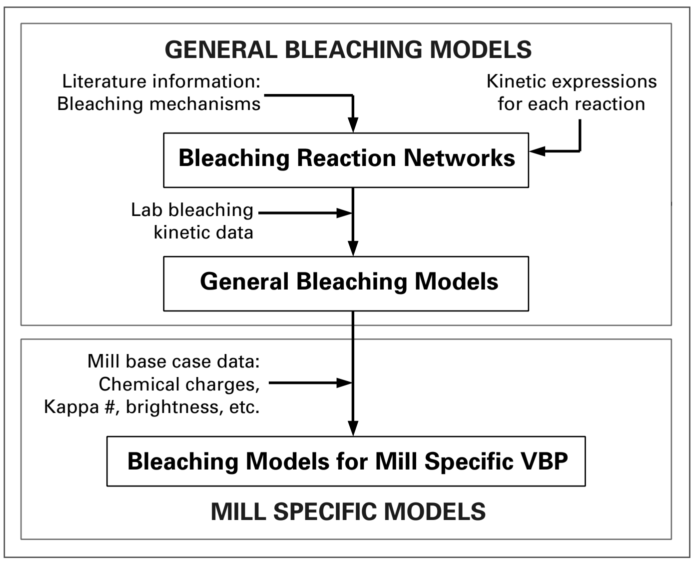
In the current VBP, we base scale prediction and NPE distribution on equilibrium calculations. We combine bleaching models with equilibrium calculations to predict bleach plant pH profiles. Using VOC simulation tools, we also can predict air emissions. **Figure 1** shows the basic components in the VBP.

VBP applications

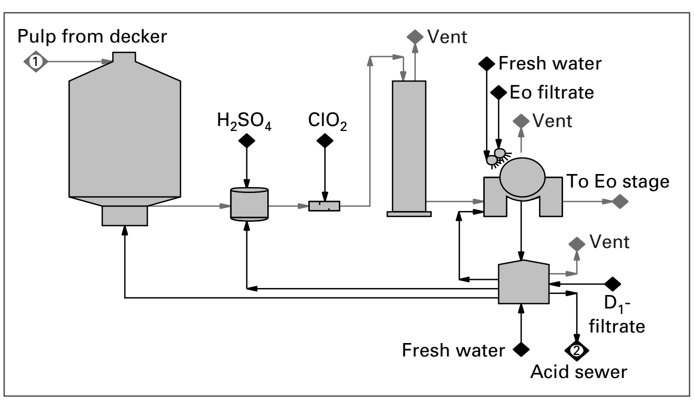
When a bleach plant is "duplicated" as a model in the VBP simulation, the simulation can be used for process analysis and other information related work. The VBP simulation provides more technical details than any model ever built for bleach plant simulation. Potential applications include the following:



1. Virtual Bleach Plant components.



2. Predictive bleaching models for mill-specific VBP simulation.



3. D_0 stage simulation interface.

1. *Evaluation of mill process alternatives:*
   - Peroxide reinforcement in extraction
   - Bleaching chemical optimization
   - COD carryover impacts
   - Filtrate recycle impacts.
2. *Evaluation and selection of capital investment options:*
   - Better washing or high carryover (i.e. high chemical consumptions)
   - Large tower or high chemical charges
   - Debottlenecking.
3. *Use as a whole bleach plant software sensor:*
   - Predict variables that are difficult to measure
   - Find measuring instrument malfunctions.
4. *Use as research and bleaching technology transfer tool:*
   - Consolidate laboratory bleaching data into model parameters
   - Compare laboratory results with historical information
   - Combine laboratory experimental results to simulate mill situations, such as effects of bleaching filtrate recirculation on chemical consumption
   - Evaluate the performance of new technologies in bleaching sequences.

Predictive bleaching models

In bleaching literature, a significant amount of information is available in the following areas:

- Bleaching mechanisms
- Kinetic data and models
- Overall bleaching results for single stages or bleaching sequences.

Because of the complexity of bleaching chemistry, it is very difficult to compare bleaching results from different researchers. Using a comprehensive modeling approach, we are able to consolidate bleaching theories and data. The results are quantitatively summarized as the predictive bleaching models that are directly applicable to mill bleach plant simulation. Parts 2 and 3 of this series will present details of the predictive bleaching models that are summarized below.

The predictive bleaching models proposed in this series of papers are based on reaction networks that summarize all the important reactions among bleaching chemicals and pulp or liquor species. The reaction network does not represent bleaching mechanisms. However, it "summarizes" the reaction steps that affect bleaching rates. Reactions are included also to generate species of interest, such as oxalate for scale prediction. Each reaction provides a stoichiometric relationship among reactants and products. Therefore, the changes of these component concentrations are clearly defined. All reactions compete for bleaching chemicals. In most literature kinetic models, kinetic equations are just for fitting bleaching data; no direct relationships between kappa reduction/brightness gain and bleaching chemical consumption are developed.

Each reaction in the bleaching reaction network has its own kinetic expression. An effect of pulp lignin concentration on delignification is used to get a smooth and flexible transition from fast delignification to slow delignification (see Part 2 for the detailed equations). Using literature kinetic data, we have developed general predictive bleaching models for ClO_2, Cl_2, hydrogen peroxide, and caustic extraction.

Due to the complexity of bleaching chemistry, the predictive bleaching models in this series are probably oversimplified and current model parameters are identified from limited data. Using a general bleaching model to represent all bleaching situations may not be realistic. Wood species and cooking processes also affect bleaching. To accurately model a specific bleach plant, mill specific information has to be included in the bleaching models. At this stage in developing predictive bleaching models, a model tuning based on regular mill operating data, such as chemical charges and brightness, is still needed. **Figure 2** outlines how mill specific predictive bleaching models are developed for VBP simulation.

MILL CASES

Bleach plant simulation

To demonstrate the abilities of the VBP, we applied it to two mill bleach plants.

Case A: "Duplicate" a DEoDED bleach plant. An ECF mill bleach plant is modeled by the VBP. Various predicted variables are compared with mill measurements and we demonstrate the modeling capacity of the VBP.

Case B: Evaluate bleach plant alternatives. VBP simulation predicts the bleaching results of DEoDED and DEopDED sequences, as well as the current mill C/DEoDED sequence for softwoods and hardwoods. The predictions are compared with mill measurements and we demonstrate that current VBP models can assist in evaluating mill alternatives.

Predictive bleaching models and other related models used in the simulation have been implemented in commercial process simulation software, WinGEMS (2). All simulation results presented in this paper are performed in WinGEMS. The bleaching models can also be implemented in any other process simulator.

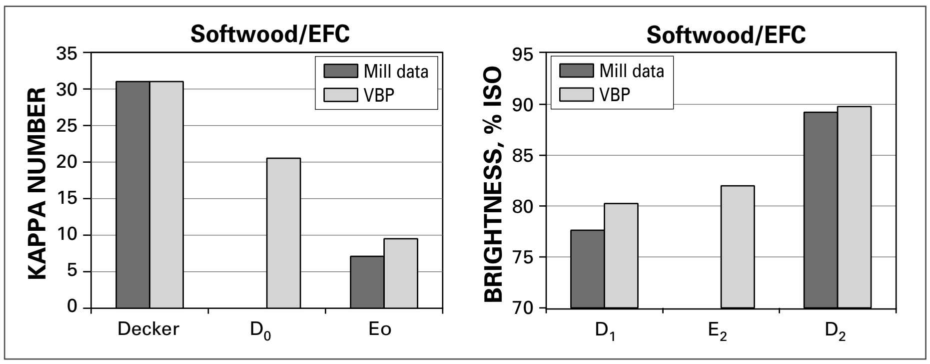
Case A: "Duplicate" a DEoDED bleach plant

The simulated bleach plant is a southern U.S. softwood kraft pulp mill. The two-vessel Kamyr digester uses Lo-Solids™ cooking technology. Brownstock washing includes a pressure diffuser, a two-stage atmospheric diffuser, a drum washer, and a decker. The bleach plant has a typical DEoDED sequence. Bleach plant incoming kappa for softwood is about 30. Pulp dryer white water is partially applied on the D_2 washer. D_2 filtrate is applied to the E_2 washer shower and E_2 filtrate to D_1 washer shower. D_0 and Eo washers have split shower bars. E_2 filtrate is used on Eo bottom shower bars and D_1 filtrate is used on Eo top shower bars. Fresh water is used on D_0 bottom shower bars and Eo filtrate on D_0 top shower bars.

INPUT STREAMS	mt/ADTP	OUTPUT STREAMS	mt/ADTP
Pulp in	8.2	Pulp out	7.6
Chemicals	3.6	Acid sewer	15.3
Fresh water	8.9	Alkaline sewer	4.0
PW white water	5.8	—	—
Steam	0.4	—	—
Total inputs	**26.9**	**Total outputs**	**27.0**

	Shower flow mt/ADTP	Mat consistency, %	Dilution factor	Seal tank mt/ADTP	Tower temp., °F	Steam usage mt/ADTP
D_0	5.19	10.5	-2.37	15.33	142	—
Eo	4.72	12.2	-1.47	3.98	170	0.14
D_1	4.84	13.1	-0.70	6.99	143	0.04
E_2	5.61	11.2	-1.02	-2.39	168	0.09
D_2	5.78	10.6	-1.46	2.63	164	0.13

I. Simulation summary: "water" and energy balance.

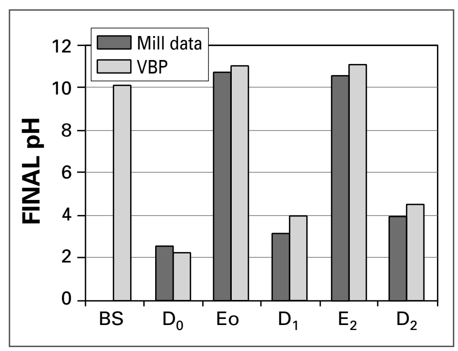


4. Comparison of kappa numbers and brightness.

The whole bleach plant is simulated as part of a full mill simulation. **Figure 3**, which is a simplified flow diagram, shows the interface of the D_0 stage simulation. Each icon in Fig. 3 includes several simulation calculation blocks. We used similar interfaces for the Eo, D_1, E_2 and D_2 stages. The simulation is organized as a process diagram.

"Water" and energy balance. Due to filtrate recirculation, the "water" balance in bleach plants is not straightforward. The variation of washer mat consistencies (**Table I**) makes the picture more complicated. Good water management can reduce bleach plant sewer flows and steam usage.

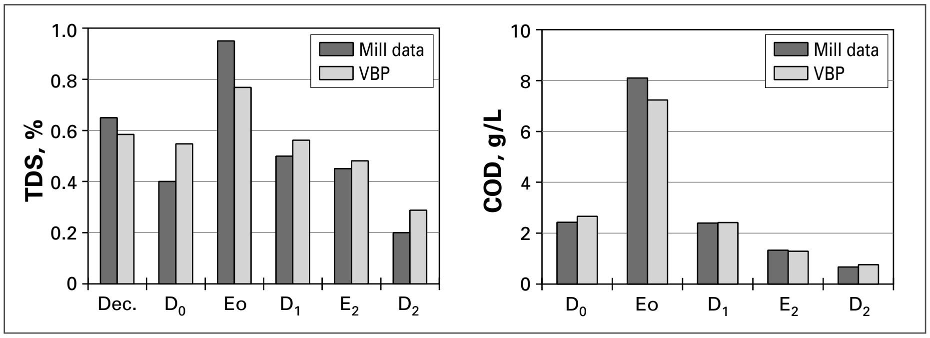
Table I summarizes the "water" balance. The overall bleach plant sewer is 19.3 metric tons/air dried ton of pulp (ADTP), of which 16.3 metric tons/ADTP is from the acid sewer. Fresh water is used on D_0 and D_2 showers. Also, 2.39 metric tons/ADTP of fresh water is added to E_2 seal tank, which could be



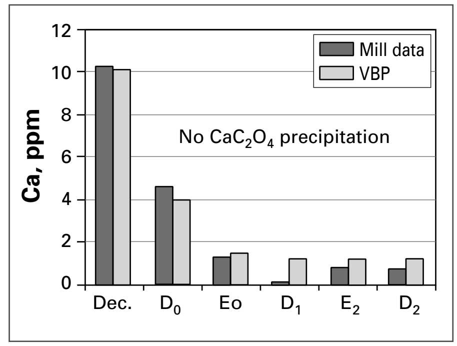
5. Bleach plant pH profile.

eliminated by better filtrate management. E_2 filtrate is used on all D_1 shower bars and Eo bottom shower bars. The mat consistency difference between D_1 (13%) and E_2 (11%) also causes 1.3 metric tons/ADTP of water addition to E_2 seal tank. A significant amount of water (3.8 metric tons/ADTP) is added from ClO_2 solution. The impact of steam on the "water" balance is small.

Measured bleach plant temperatures match the simulation (Table I). Steam usage for each steam mixer, shown in



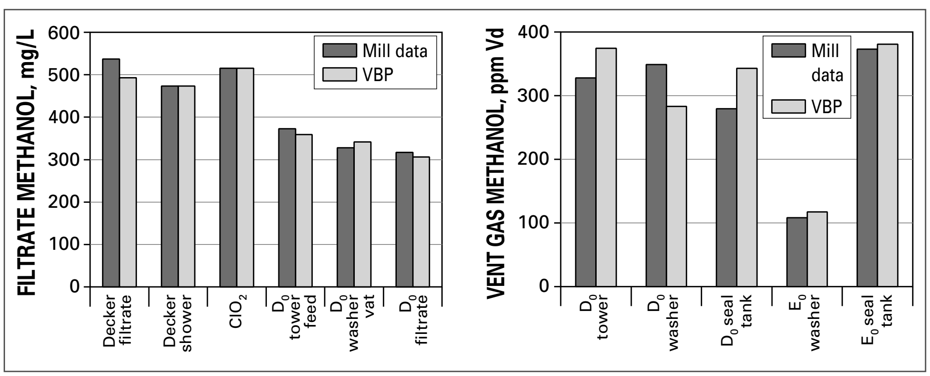
6. Total dissolved solids (TDS) and COD in bleaching filtrates.



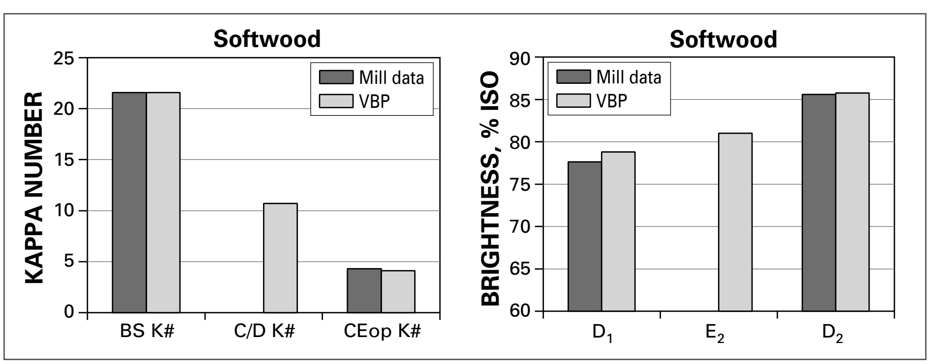
7. Calcium profile in ECF bleach plant.

	CHLORIDE		CHLORATE		SULFATE		TDS		COD	
	Mill data mg/L	VBP mg/L	Mill data mg/L	VBP mg/L	Mill data mg/L	VBP mg/L	Mill data %	VBP %	Mill data g/L	VBP g/L
Decker	18	20	0	0	205	165	0.65	0.58	8.68	9.29
D_0	790	780	390	382	725	959	0.40	0.55	2.42	2.66
Eo	510	514	170	213	295	459	0.95	0.77	8.10	7.23
D1	1150	1094	615	512	105	120	0.50	0.56	2.40	2.42
E2	450	612	245	237	54	47	0.45	0.48	1.33	1.29
D2	500	557	315	164	50	17	0.20	0.29	0.67	0.76
WW	175	309	18	91	39	9	0.08	0.16	—	—

II. Mill-measured and VBP-predicted filtrate compositions.



8. Methanol concentrations in bleaching filtrates and vent gases.



9. K Number and brightness profile for 65% ClO_2 substitution.

Table I, is computed by matching stream temperature changes.The simulation also shows that all bleach plant washers have negative dilution factors. Therefore, carryover between stages is a problem.

Kappa and brightness. The development of brightness in a bleaching sequence is more closely related to chemical consumptions than is the final brightness. In order to optimize the operation of a bleaching sequence, the model needs to predict kappa number or brightness for each stage. **Figure 4** compares simulation predictions with mill measurements. Normally, final D_0 kappa is not measured during operations. However, it is critical to control D_0 final kappa for the optimization of chemical applications (ClO_2 and caustic) in a bleaching sequence.

pH profile. Caustic is consumed in extraction stages and acid is generated in ClO_2 bleaching. The bleaching models include these effects. Pulp and bleaching filtrates also have pH buffering capacity. An equilibrium model has been developed to represent these buffer effects (7). The prediction of pH profile in bleach plants is the combination of bleaching models and equilibrium calculations. **Figure 5** shows the simulation results. Because pH is used as an indicator for caustic and/or acid charges, it is important to know pH changes in bleach plants. A better measurement for extraction stage caustic charge is alkalinity, instead of pH, because hydroxide is the major active component that is responsible for extraction.

Filtrate composition. During bleaching, pulp is partly converted into various dissolved components. These dissolved components are related to filtrate measurements, such as total dissolved solids (TDS) and COD, and are used in various process analyses, such as scale prediction. About 35 aqueous species have been included in the bleaching models. More species can be added if they are identified from bleaching research. A COD model has been developed to compute filtrate COD from the concentrations of dissolved organics. The model-predicted TDS and COD for filtrate from each stage are compared with mill measurements in **Fig. 6**. More bleaching filtrate compositions are compared with mill measurements in **Table II**. The concentrations of all the built-in species for all the streams in the simulation are available. Since the models predict dissolved components from bleaching, yield loss is available for all stages.

The filtrate concentrations of aqueous species can be calculated from mass balances if the generation of these species during bleaching is available. Some generation models, such as those for methanol (4) and oxalate (5), are available in the literature. Methanol generation during bleaching has been connected to lignin dissolution and included into the bleaching models (9). By including the generation models into the bleaching models, the effects of bleaching conditions are included. Through simulation, mill filtrate measurements can be converted into generation rates. Converting concentrations into generation rates removes the effects of process configurations. Thus, generation data are more reliably transferred from one mill to another.

Metals profiles. By inserting the metals equilibrium calculation block (8) into bleach plant models, the simulation predicts metals profiles. Ca, Na, Mg, K, and Ba are included in Case A. The equilibrium calculation also checks the solubility of CaC_2O_4, $CaCO_3$ and $BaSO_4$. When the concentrations of these species are higher than their solubility, potential precipitation is identified. The model predicted Ca profile is compared with mill measurements in **Fig. 7**. The model predicts no calcium precipitation as CaC_2O_4 or $CaCO_3$. Profiles for other modeled metals are also available from the simulation.

The metals equilibrium calculation is conducted in a different simulation block from the bleaching models, although oxalate and carbonate generation during bleaching are included in the bleaching models. The equilibrium calculation can be turned off in the simulation if it is not needed.

Methanol air emissions. Methanol filtrate concentrations in bleach plants are calculated from methanol generation and brownstock carryover. Methanol generation in bleach plants (9) has been included in the predictive bleaching models. Recently developed VOC models (6) predict air emissions as a function of filtrate concentrations and temperatures. **Figure 8** compares VBP predictions with mill measurements for methanol. The air emissions of other VOC species can also be predicted. VOC air emission prediction is also conducted in separate blocks that can be turned off if not needed.

Case A summary. In Case A, a real bleach plant is "duplicated" by the VBP simulation. The backbone of the VBP is a process model with bleaching kinetics included. The process model represents the real mill process configuration and operating conditions. The kinetic bleaching models predict what is happening in the bleaching towers. The backbone model predicts brightness, chemical consumptions, filtrate compositions, carryover impacts, peroxide reinforcement effects, etc. The backbone model addresses the daily concerns of bleach plant operations and economics. On the backbone model, additional models are attached to address more special issues, such as scale formation and VOC air emissions. The Case A results shown above derive from only one WinGEMS model. All data from the simulation are output into an EXCEL file. Then, information is selectively organized to address specific issues and presented in a user-friendly format, as in Figs. 4-8.

	MILL DATA[1,2]	VBP, C/D[2]	VBP, D_0[3]
C/D stage	57.8%	57.7%	51.6%
Eop stage	68.9%	64.9%	68.6%
C/D & Eop stage	86.8%	84.8%	84.5%

[1] From limited lab measurements for C/D and Eop stages.
[2] 65% ClO_2 substitution at C/D stage.
[3] 100% ClO_2 substitution.

III. Softwood kappa reductions in C/D, D_0, and Eop stage.

Mill databases have been widely used in the pulp and paper industry. If VBP simulation inputs are connected to a mill database, simulation can be done continuously. In this way, the simulation acts as an online software sensor for the whole process. Measured variables are checked by the simulation and measurement problems can be pinpointed. Unmeasured variables are estimated continuously by the simulation. Process performance evaluation is also available from the simulation. Problems in processes and operations can be identified more quickly using the VBP as a soft sensor.

Case B: Evaluate bleach plant alternatives

Using mill operating data, the new predictive bleaching models are tuned for this specific bleach plant. This mill-specific Virtual Bleach Plant model is then used to optimize chemical charges for ECF bleaching and consider peroxide reinforced extraction.

The results of both softwood and hardwood ECF simulations are presented.

Base case. The simulated bleach plant is from a northern U.S. kraft pulp mill. The bleaching sequence is C/DEopDED. In 2000, the C/D stage was running at 65% ClO_2 substitution based on active chlorine. The mill runs softwoods and hardwoods. The kappa for softwoods entering the bleach plant is 33 on average and 18 for hardwoods.

In the simulation, bleaching chemicals are charged the same as for actual mill operations. Some kinetic parameters are adjusted to match mill data. **Figure 9** shows the comparison of mill data with VBP prediction for softwood K number and brightness. The final K number of the C/D stage was collected to validate the VBP simulation. **Table III** shows the comparison. The mill operation for softwood with 65% ClO_2 substitution is well represented by the VBP simulation.

ECF softwood bleaching. After the VBP is tuned, softwood ECF bleaching is predicted by VBP simulation without further tuning. **Table IV** shows the simulation results and mill data for ECF operation. We adjusted the chemical charges for ECF bleaching in the mill operation, as shown in Table IV. In the VBP ECF simulation, we again match the chemical charges to mill applications. Table III lists the degree of delignification in D_0 and Eop. Although the total delignification from D_0 and Eop is not changed, the split of delignification between D_0 (or C/D) and Eop has been changed.

Table IV shows that ECF takes 11% more total ClO_2 than C/D with 65% ClO_2 substitution. The mill chemical charges for ECF bleaching are not optimized. With VBP simulation, better chemical charges have been found. Currently, the mill plans to conduct mill trials based on optimized chemical charges from the VBP simulation.

	CHARGE CHANGES[1]		C/D SEQUENCE[2] Mill data	C/D SEQUENCE[2] VBP	ECF SEQUENCE Mill data	ECF SEQUENCE VBP
C/D, active Cl	13.4%	Decker K number	21.6	21.6	21.9	21.9
Eop, caustic	-6.8%	CEop K number	4.3	4.1	4.2	4.3
D_1, ClO_2	7.7%	D_1 brightness, %	77.6	78.8	79.1	78.2
E_2, caustic	15.8%	E_2 brightness, %	—	81.0	—	80.6
D_2, ClO_2	9.5%	D_2 brightness, %	85.6	85.7	85.8	85.7
Total ClO_2	11.2%					
Total caustic	0.4%					

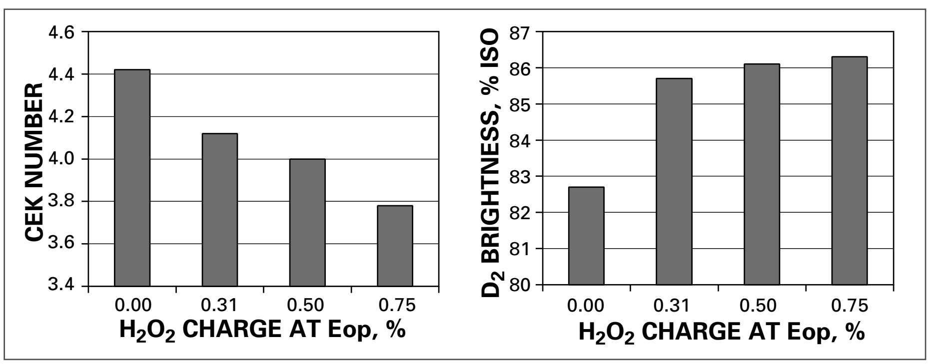
[1] C/D sequence as the basis. Not % on pulp. [2] 65% ClO_2 substitution at C/D stage.

IV. Predictions for softwood ECF bleaching relative to 65% ClO_2 substitution.

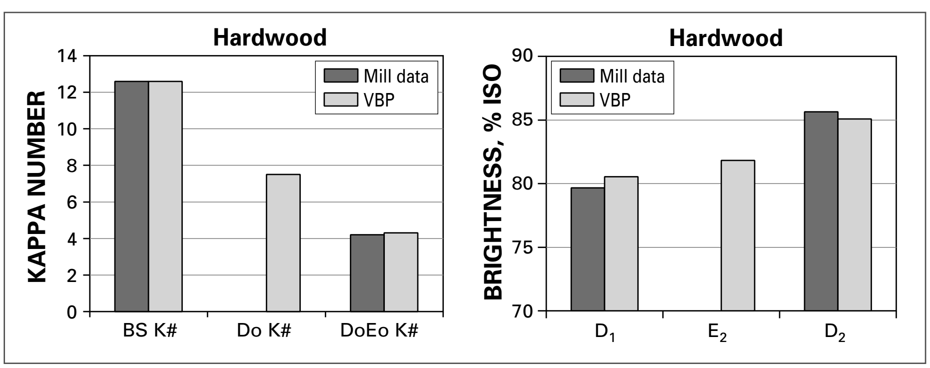
	CHARGE CHANGES[1]		0.31% H_2O_2 at Eop[2] Mill data	0.31% H_2O_2 at Eop[2] VBP	No H_2O_2 AT Eop[2] Mill data	No H_2O_2 AT Eop[2] VBP
C/D, active Cl[2]	-0.1%	Decker K number	21.6	21.6	22.1	22.1
Eop, caustic[3]	2.0%	CEop K number	4.3	4.1	5.4	4.8
D_1, ClO_2	28.3%	D_1 brightness, %	77.6	78.8	75.3	77.3
E_2, caustic	26.3%	E_2 brightness, %	—	81.0	—	80.2
D_2, ClO_2	15.8%	D_2 brightness, %	85.6	85.7	85.1	85.5
Total ClO_2	11.2%					
Total caustic	9.7%					

[1] Case of 0.31% H_2O_2 charge as the basis. [2] 65% ClO_2 substitution at C/D stage. [3] 0.5% O_2 charge at Eop/Eo.

V. Validation of softwood peroxide reinforcement impact.



10. Predicted peroxide impact at fixed bleaching conditions (softwood), except peroxide charge.



11. Hardwood ECF bleaching simulation.

Peroxide reinforced extraction (softwood). Currently, the mill is applying 0.31% H_2O_2 on pulp at the Eop stage for softwoods. Mill operating data for no H_2O_2 charge at Eo were collected to test the VBP's ability to predict the effects of peroxide reinforcement. **Table V** shows the simulation results and mill data. The case with no peroxide at Eop takes 11% more ClO_2 and 10% more caustic.

Fixing all other chemical charges and other bleach plant operating conditions, the VBP model predicts the impact for peroxide reinforcement at the Eop stage, as shown in **Figure 10**.

Hardwood ECF bleaching. Using the same bleaching model structure as softwoods, model parameters for hardwoods are tuned according mill operating data. **Figure 11** shows the simulation results for hardwoods ECF bleaching.

CONCLUSIONS

Modular mass and energy balance simulation systems (e.g. WinGEMS) have been used for simple bleach plant calculations (flows, consistency, temperature) for at least 30 years. For well over a decade, University of Idaho researchers have been working to develop practical, predictive bleaching models. Now, comprehensive models that calculate pulp brightness, scale formation, VOC emissions, filtrate pH and effluent COD have been added to WinGEMS to produce the Virtual Bleach Plant (VBP). This paper validates the VBP using real mill data and successfully demonstrates the VBP's ability to address real mill problems (e.g. minimum cost conversion to ECF bleaching.) **TJ**

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INSIGHTS FROM THE AUTHORS

Why did you choose this topic to research?

The industry needs tools to help evaluate mill bleach plant alternatives.

Explain how this research either complements and supports previous research you (or others) have done or how it differs from previous research.

The work continues our 10-year bleach plant kinetic modeling effort.

What was the most difficult aspect of this research and how did you address that?

Bleaching chemistry is very complex so we had to develop the "reaction network" approximation.

What did you personally discover from this research? What was most interesting or surprising about your findings?

The simulation can address real mill issues, such as alternative filtrate configurations.

How might mills benefit from or use this information?

Evaluation of economics, environmental and product quality issues are facilitated by the VBP.

What's the next step?

Apply the VBP to more mill cases so it can be improved.

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