Study of a model of cellulose depolymerization in the hypochlorite bleaching stage

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ABSTRACT *The possibility of developing a useful model for controlling the viscosity decrease during hypochlorite bleaching was studied. This led to a simple and practical model capable of predicting final viscosity, despite the use of various approximations. The model takes into account the linear and quadratic effects of starting viscosity, and linear and logarithmic effects of hypochlorite charge. The effects of pH, temperature, and pulp consistency were also considered and were introduced into the main model in the form of a corrective equation.*

KEYWORDS
Analysis
Bleaching
Chemical analysis
Cellulose
Mathematical models
Viscosity

The purpose of this work was to develop a model to correlate the viscosity decrease during the hypochlorite stage with all process parameters involved in such a way as to allow effective control of the final viscosity of dissolving pulps. The model had to be suitable for automation of the hypochlorite stage, to make it possible to obtain preselected and constant viscosity values.

The process we considered involved European hardwood sulfite normal and rayon-grade dissolving pulps, using the bleaching sequence (C+D) E (D/H). The H stage was carried out in a sequence of three up-flow towers, each capable of accepting reagents at the bottom.

The influence of pulp consistency

A range of consistency between 7% and 14% was studied. This range covers almost all possible fluctuations of consistency in an industrial plant working at medium consistency.

The results are shown in **Fig. 1**. Variations of consistency do not influence the final viscosity at constant initial viscosity, temperature, pH, and initial concentration of active chlorine. This evidence is in agreement with the works of Wolfrom (*1*) and Lekander (*2*), showing that the kinetics of oxidation of cellulose (related to depolymerization) is of zero order with respect to cellulose.

However, the efficiency of the reaction, measured by the ratio of viscosity decrease ΔV and hypochlorite consumption ΔC, is influenced by the consistency. Plotting $\Delta V / \Delta C$ vs. the consistency, as shown in **Fig. 2**, the linear relationship with consistency becomes apparent.

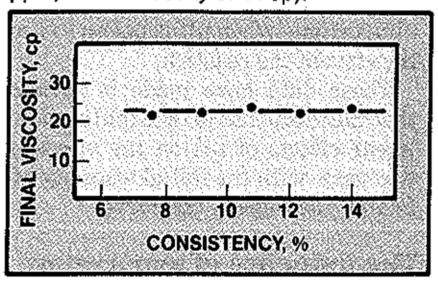
Chlorine consumption, which is also influenced by the brightening reactions, obviously depends upon the cellulose concentration.

The effects of pH and buffering

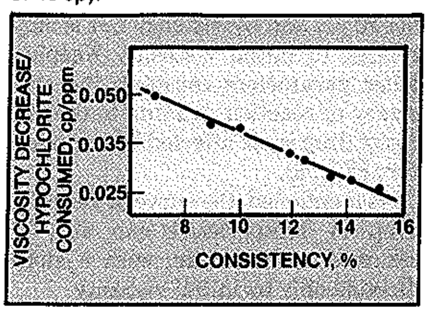
The depolymerization rate is of course strictly related to pH. Our experimental data show that the decrease in viscosity vs. pH (other parameters being constant) is related to initial viscosity. **Figure 3** shows that hypochlorite charge has a negligible effect on this ratio. Thus, the slope of final viscosity vs. pH is constant at different hypochlorite concentrations.

Figure 3 and **Fig. 4** also suggest the usefulness of buffering for maintaining linearity of the ratio of viscosity vs. pH. However, in industrial practice, the deviation from linearity resulting

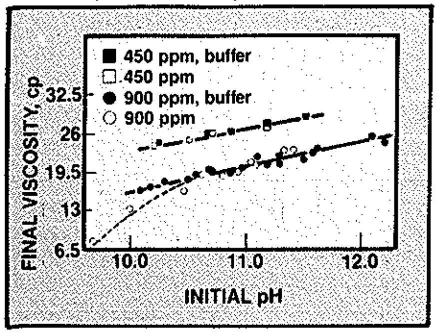
1. Consistency variations do not influence the final viscosity (initial active Cl_2 of 825 ppm, initial viscosity of 44 cp).



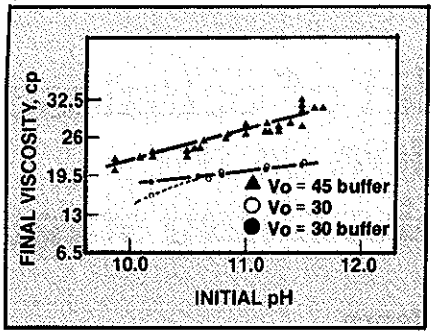
2. Hypochlorite consumption is directly influenced by consistency (initial viscosity of 46 cp).



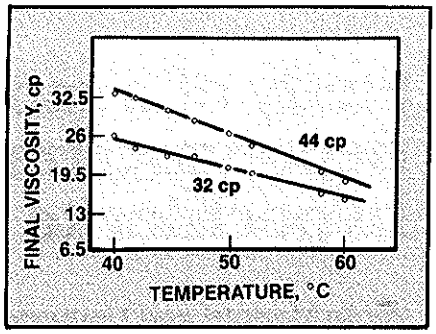
3. The slope of final viscosity vs. pH is constant at different hypochlorite concentrations (initial viscosity of 35.5 cp).



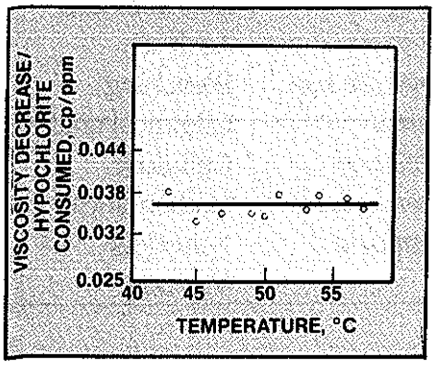
4. Buffering is effective in maintaining the linearity of the ratio of viscosity vs. pH (initial active Cl_2 of 675 ppm)



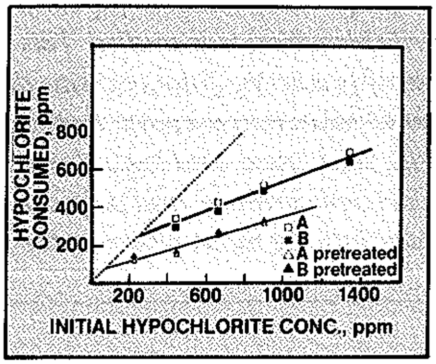
5. The relationship between viscosity decrease and temperature is linear (initial active Cl_2 of 675 ppm).



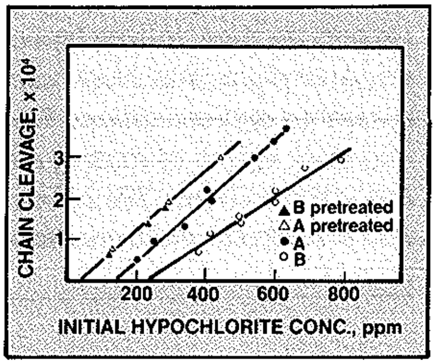
6. Keeping other factors constant, the efficiency of reactions leading to viscosity drop is not affected by temperature (initial active Cl_2 of 900 ppm, initial viscosity of 46 cp)



7. The intercept with the the dotted line can be regarded as a "purity index."



8. The number of chain scissions is related to the amount of hypochlorite consumed.



from insufficient buffer becomes significant only when pH is below 10.6 at the start of the reaction.

These data have made it obvious that the model has to take into account linear effects of pH on the viscosity decrease, with the initial viscosity affecting the slope of the curve.

The influence of temperature

The relationship between viscosity decrease and temperature is linear, as shown in **Fig. 5**. Its slope is related neither to concentration of hypochlorite nor to pH and consistency but is only related to initial viscosity Keeping other parameters constant, the efficiency of reactions leading to the viscosity drop is not affected by temperature **(Fig. 6)**.

As mentioned, the curve of viscosity drop vs. temperature can also be assumed to be linear, with a slope dictated only by initial viscosity.

Pulp purity, brightness, and hypochlorite consumption

We followed methods used by Herbst and Krassig (*3*) and Paulson (*4*) for studies on purity and brightness.

Given in **Fig. 7** are straight lines showing hypochlorite consumption of various samples. As stated by Paulson (*4*), the intercept between these lines and the dotted line, which represents the total consumption of hypochlorite, is related to the rapid consumption of hypochlorite caused by reactions with lignin. This intercept can be regarded as a "purity index."

In **Fig. 8**, the number of chain scissions, or cleavages, is related to consumed hypochlorite:

$$\text{scissions} \propto 1/DP - 1/DP_0 \qquad (1)$$

where

DP = degree of polymerization
DP_0 = initial degree of polymerization.

According to Herbst and Krassig (*3*), the graph gives us information about the lignin and hemicellulose contents of various pulps. The intercept with the abscissa is correlated with lignin, and the slope correlates with the concentration of hemicellulose and lignin.

The wood pulps show differences in behavior, but these differences disappear if the pulp is pretreated with hypochlorite. In comparison with the data reported by Paulson (*4*), our samples appear to be rather pure, allowing us to conclude that the reactions competing with pulp depolymerization are of no great influence. In building a model, the purity of the pulp has to be taken into account in the computation of hypochlorite consumption.

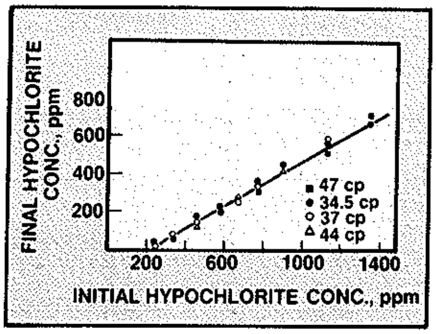
Assuming that the kinetics of cellulose depolymerization are first order with respect to hypochlorite concentration and that hypochlorite consumption in bleaching reactions takes place in the first minutes of reaction, the following empirical equation was developed from kinetic data **(Table I)** experimentally obtained from pulps of different initial brightnesses:

$$C_f = C_0 - [910 - (9.2 \times B)]\, e^{-0.28t} \qquad (2)$$

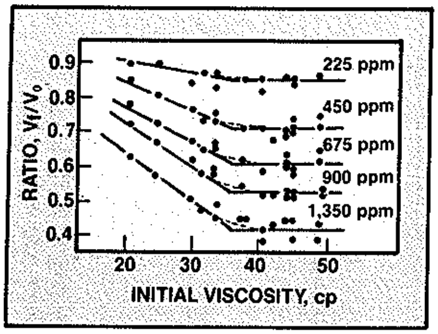
where
C_0 = initial concentration of active chlorine in the liquid phase
C_f = final concentration
B = Elrepho brightness, %
t = time.

The term between internal parenthe-

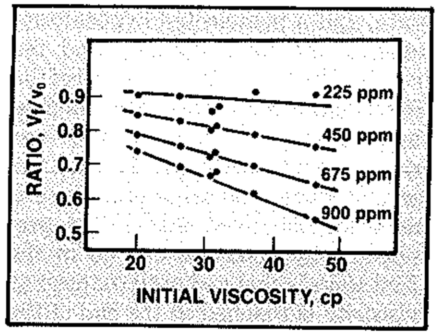
9. The starting viscosity has no influence on hypochlorite consumption.



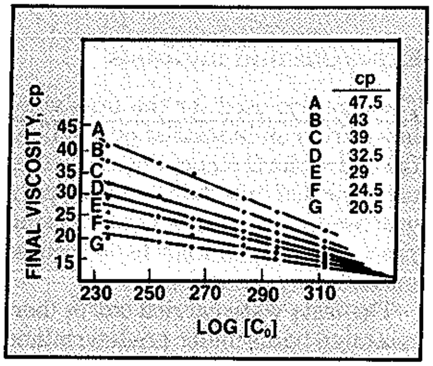
10. The ratio of final viscosity:initial viscosity, vs. the initial viscosity for Pulp A.



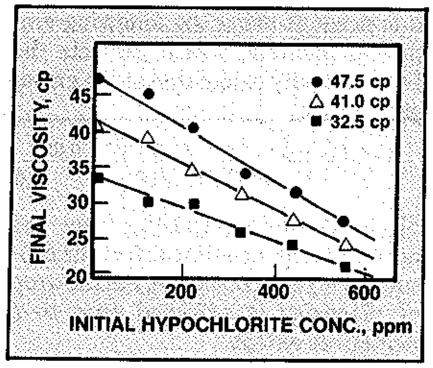
11. The ratio of final viscosity:initial viscosity, vs. the initial viscosity for Pulp B.



12. When the hypochlorite is not completely consumed, the final viscosity is a function of the logarithm of the initial hypochlorite concentration.



13. When the hypochlorite is totally consumed, the dependence of final viscosity on initial hypochlorite concentration is linear.



I. Results of experiments on pulps of different initial brightness

	Test 1	Test 2	Test 3
Residual hypochlorite, ppm			
0 min	700	700	700
30 min	468	489	539
60 min	363	404	479
90 min	319	358	429
120 min	308	326	363
180 min	199	...	291
240 min	184	174	...
300 min	124	131	198
420 min	53	71	...
Initial brightness, %	82.6	84.5	88.0

sis represents the rapid hypochlorite consumption by lignin. The process conditions used in developing this equation were: T = 52°C, pH = 10.8, consistency = 10%. The equation is valid in the brightness range of 80% to 90%.

The starting viscosity can be assumed to have no influence on hypochlorite consumption, as shown in **Fig. 9.**

The effect of hypochlorite charge on initial viscosity

The relationship between viscosity decrease at different hypochlorite charges and starting viscosity is rather complex. The results of several experiments are shown in **Figs. 10 and 11.**

In the range of starting viscosity values we studied, pulps made from two different types of wood behave differently. The relationship between final viscosity and starting viscosity of Pulp A can be assumed to be linear for a starting viscosity above 35 cp, whereas it will be quadratic below that value. For Pulp B, only a quadratic relationship was indicated. Probably Pulp B would also show a linear behavior at an initial viscosity exceeding 45 cp, which was outside the range we examined. At the moment, we are not able to explain the different behavior of the two pulps.

The final viscosity is related to hypochlorite charge in different ways, depending on whether hypochlorite consumption is complete or a residual is left at the end of the chosen reaction time. When the hypochlorite is not completely consumed (**Fig. 12**), the final viscosity is a function of the logarithm of the initial hypochlorite concentration.

On the other hand, when the hypochlorite is totally consumed (**Fig. 13**), the dependence of final viscosity on initial hypochlorite concentration is linear.

These findings agree with those of Rutkowsky (*5*), who found a linear dependence at low hypochlorite charge and a lower-order dependence when the dosage was higher.

Building a mathematical model

Basic conditions

The number of hypochlorite stages is assumed to be 3. The residence time of each stage is 2 h. The previous bleaching sequence is (C+D)ED.

The pH is 10.8. At the beginning of each stage, the pH is restored to 10.8 by adding the necessary amount of sodium hydroxide. There is no buffering. The temperature is held constant at 52°C throughout all the stages.

The consistency is 10%. A fluctuation between 9% and 11% is allowed, because it does not seriously impair the validity of the model.

The input data requested are:

- Incoming viscosity
- Incoming brightness
- Desired final viscosity
- Type of wood used.

The output of the model will be the concentration of hypochlorite in the liquid phase, to be established at the beginning of the first stage.

Structure

The model calculates, using actual incoming viscosity, actual brightness data, and a preselected hypochlorite charge, the final viscosity and the residual hypochlorite at the end of the first stage. Final viscosity and residual hypochlorite calculated in the first stage are used as input data for the second stage. The same procedure is used for the third stage. The preselected hypochlorite charge in the first stage is changed until the desired viscosity is reached at the end of the third stage.

Algorithms used

In the case of pulp made out of Wood A, the equations are:

$$C_f = C_0 - [910 - (9.2 \times B)] e^{-0.28t} \quad (2)$$

$$V_f = V_0 - C_0 (-0.455 \times 10^{-2} + 8.1 \times 10^{-4} V_0) \text{ if } C_f < 40 \text{ ppm} \quad (3)$$

$$V_f = V_0[0.940 + V_0 \times (3.833 \times 10^{-2} - 1.682 \times 10^{-2} \times \log(C_0)] \text{ if } V_0 > 35 \text{ cp and } C_f > 40 \text{ ppm} \quad (4)$$

$$V_f = V_0 - 2.162 - 0.554 \log(C_0) \text{ if } V_0 < 35 \text{ cp and } C_f > 40 \text{ ppm} \quad (5)$$

II. Results of the check runs on model predictions

C_0	V_0	B	Final viscosity: Calculated	Final viscosity: Experimental
300	29.8	86.8	23.8	24.2
400	29.8	86.8	20.8	20.8
500	29.8	86.8	19.6	19.9
500	29.8	86.8	19.6	19.5
700	29.8	86.8	16.4	16.3
600	41.5	82.3	21.7	22.4
900	41.5	82.3	16.0	19.9
900	41.5	82.3	16.0	16.0
1.000	48.1	84.4	17.2	18.2
300	49.7	85.8	37.0	35.6
600	49.7	85.8	25.3	25.1
1.000	49.7	85.8	17.6	16.6

Slight deviations from the conditions of temperature and pH can be taken into account using the following empirical formula, which corrects the final viscosity calculated at the end of each stage:

$$V_f = V_f - 2.50 \times 10^{-2} V_0 (T - 52) + 0.335 (V_0 - 20)(\text{pH} - 10.8) \quad (6)$$

Slight deviations (±10%) from the normal residence time affect the consumption of hypochlorite, but the drop of viscosity is affected only to a negligible extent.

Check of the model

The prediction capacity of the model was tested by running several batches of pulp through the pilot plant. Different brightnesses, viscosities, and hypochlorite charges were checked. The results are expressed in **Table II**, which shows that the agreement is satisfactory.

Final remarks

This work was aimed at developing a simple empirical model to simulate the decrease in viscosity during hypochlorite bleaching.

The algorithm we have developed and used does not necessarily have a physical significance. Further studies will be necessary to demonstrate and eventually understand the true meaning of the dependence of the viscosity drop on the square of starting viscosity or on the logarithm of hypochlorite charge. Nevertheless, the model obtained is simple and handy. If coupled with sensors for brightness and hypochlorite charge, it would be suitable for purposes of automating hypochlorite bleaching stages and would enhance our capability of controlling final viscosity in dissolving pulp production.

Experimental methods

The samples used for the tests were taken from an industrial pulp mill at the end of the D stage. For viscosities not typical of industrial settings, pulp was prepared in the pilot plant using procedures as similar to industrial methods as practicable.

The tests were carried out in thermostated baths under predetermined conditions of pH, consistency, chemical charge, etc. After the appropriate reaction time, the pulp was washed and tested for viscosity.

Viscosity was measured in a cuprammonium solution according to TAPPI method T 206. All other analyses were performed using common procedures.

As mentioned, the bleaching parameters were studied under the following conditions: 52°C, 11% consistency, pH = 10.8, and time = 2 h.

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Received for review Jan. 5, 1987.

Accepted Aug. 4, 1987.

Presented at the 1987 Dissolving Pulp Conference.