The buildup of dissolved solids in closed white water systems

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ABSTRACT: A mathematical model has been developed to predict how the dissolved solids will build up after the white water system of a paper machine is closed to different degrees. In the closing of a mill system, any reduction in the paper machine water consumption will be accompanied by an increase in the dissolved and colloidal solids in white water. According to the model, the dissolved solids coming into the system will not build up endlessly, no matter how many times they are recycled and how tightly the system is closed. The final equilibrium concentration of any dissolved solids will be less than the flow-proportional average concentration of that species in all outside water sources entering the system. Laboratory experimental results were in fair agreement with the model predictions.

Application: A mathematical model can predict the buildup of dissolved solids in a closed white water system.

The consumption of fresh water is not only an environmental concern but also an issue of costs. The water coming into a mill costs money, and treating the water to the point that it is permissible to discharge costs money as well. Closing the water system can reduce raw material costs as fiber and filler materials are recovered. In addition, heat is conserved in water reuse, reducing fuel consumption and increasing both operating efficiencies and production rates [1].

Our objective was to further develop a mathematical model that reflects an understanding of how the dissolved solids build up once the mill is closed or as it is closed further. The model was tested using results from simulated laboratory closure experiments. The model can be used to produce results that may give the papermaker more information before a decision is made to further close the mill.

BUILDUP OF SUBSTANCES IN MILL CLOSURE

The white water system contains various dissolved inorganic and organic substances. A comprehensive summary about these substances was published in 1979 [2]. In an "open" water system, where a relatively large percentage of the water is discharged, there is a continuous and substantial purge of dissolved substances from the system. As the mill closes the water system by recirculating a greater percentage of its water, the dissolved substances will increase. When present in sufficient concentrations, these substances will cause production difficulties such as increased deposits, foaming, biological activity, corrosion, and poorer retention. They may also impair the physical properties of paper.

White water

During discussions of white water closure, there can be confusion as to what constitutes closure. The most common definitions of closure are based on how much of the white water is recycled. Another approach to closure focuses on the amount of fresh water consumed for the production of each unit weight of paper. In reality, fresh-water usage indirectly points to the amount of white water recycled, with low amounts of fresh water indicative of a high degree of closure. From a practical point of view, the white water recycle ratio is suitable in addressing problems restricted to the wet end, whereas absolute fresh-water consumption is a better indication when the paper mill is considered as a whole. To accurately describe a mill's progress toward closure, one should keep track of both numbers.

Understanding the solids buildup is the first step in combating problems owing to white water closure. Webb indicated that the total concentration of dissolved solids in white water would dramatically increase when the water consumption is less than 20 m^3/ton [3]. With a closed operation, the level of dissolved solids in white water can rise to 10,000 mg/L or higher [4]. In one linerboard mill using 100% post-consumer fibers (OCC and mixed waste), the total dissolved solids in white water increased to around 14,000 mg/L after fresh water usage was reduced to 1.5 m^3/ton [5]. In another linerboard mill, one using recycled gypsum, the dissolved solids rose to 15,000 mg/L after the white water system was closed [6]. However, these kinds of data are normally specific to a product or mill and cannot give a general guideline to papermakers.

EF, the enrichment factor

Alexander and Dobbins defined a term called the "enrichment factor" [7], which gives a general indication of the buildup of nonsubstantive materials in closed white water. The enrichment factor, or *EF*, was defined as the ratio of the equilibrium headbox concentration of a specific species at a particular degree of closure to that at zero degree closure. The enrichment factor can be calculated using a simple equation $EF = 1/(1 - r)$, where r is the recycle ratio, or the amount of white water recycled divided by the total amount of water to the headbox.

The enrichment factor allows one to predict the buildup of a species in the headbox as the amount of closure increases. This formula has been referred to as the basis for understanding the buildup of dissolved electrolytes in a closed paper mill system [8]. According to Alexander and Dobbins, the enrichment factor can be increased from <1 in an open system to 160 in a 100% closed headbox.

However, Alexander and Dobbins's enrichment factor did not account for the adsorption of dissolved solids on fibers. Also, though not dictated directly, one

	Tap water	Filtrate
Na^+, mg/L	5.17	522.9
Ca^+, mg/L	7.67	82.23
Mg^{++}, mg/L	1.34	10.04
Ba^{++}, mg/L	0.009	0.0516

I. Cations in tap water and thick-stock filtrate.

assumption made in the elucidation of the formula is that the fresh water used to dilute thick pulp in a zero recycling water system contains no dissolved solids of detrimental species. **Table I** presents the results of the analysis of several cations usually found in tap water and in the thick-stock filtrate used in this research.

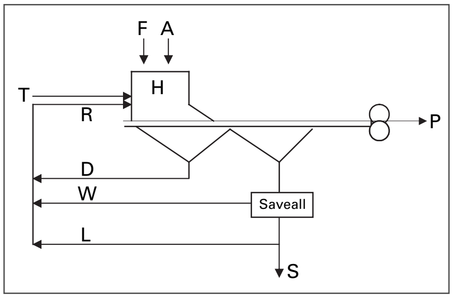
Although the solids content in fresh water is normally much lower than that in other water sources, such as thick stock, fresh water may still be a significant part of the white water, considering that fresh water may constitute 90% of the total water in the headbox in a zero recycling system. This circumstance is especially true for species that are relatively rich in fresh water, such as inorganic salts and humic acid. The calculation will give a significantly higher result than the actual measurement of these species.

MATERIALS AND METHODS

A Georgia linerboard mill supplied the furnish for the experiments. Taken right after the refiners, the furnish had a consistency of approximately 4%. A Formette Dynamique was used to generate directional, two-ply handsheets. The top furnish was 90% virgin kraft and 10% clay, while the bottom furnish was 65% virgin kraft and 35% OCC.

The thick stocks were diluted to a consistency of 0.45%, and the pH was adjusted to 5.0 with sulfuric acid and sodium hydroxide before the handsheets were made. Alum was added at 18 lb/ton. If fresh water was required, tap water was used to dilute the furnish. The bottom ply made up about 80% of the target basis weight of the two-ply sheet of 205 g/m².

After one sheet was made, the white water was saved and used as the dilution water for the next sheet. This sequence was repeated until an equilibrium condition was reached. The equilibrium condition was determined by the conductivity of the furnish. We analyzed the concentrations of sodium and calcium in the white water of selected runs using the inductively coupled plasma (ICP) technique.



1. Water flows in a paper mill.

SOLIDS BUILDUP

The design of the paper mill's stock and water system varies a lot, depending on the paper grade and the type of machine used. For simplification, waters around a paper machine can be divided into two parts: those from outside sources and those recycled inside the paper mill. Water from outside sources includes water coming in with raw materials and additives and other mill waters such as make-up water, shower water, and any cooling/seal water that winds up in the process. Water recycled includes both fiber-rich white water and lean white water after the saveall.

Figure 1 is a simplified illustration of water flows around a paper machine, similar to that used by Alexander and Dobbins. The water streams in the figure are as follows:

F = fresh water added to the manufacturing process
A = water with additives
T = water coming in with thick stock
H = water through the headbox
R = total recycled white water going back to the headbox
D = white water going back directly to the system without passing the saveall
W = white water going back to the system with recycled furnish at the saveall
L = lean water going back to the system
P = water coming off with the sheet
S = white water discharged.

Here, the headbox is an abstract concept that represents the total water flow in the system and that separates the water flow into different cycle numbers used to elucidate the model. Flows D, W, and L may be different from mill to mill. For example, part of L may be used as shower water rather than used as dilution water. However, from a water balance point of view, the final result of the water flow is equal to sending these waters directly to the headbox.

Thick stock is the incoming stock right before dilution with white water. In addition to the water streams described, an adsorption coefficient K is defined as the percentage of any species of interest X removed from the system by adsorption on fibers:

$$K = ([X_{headbox}] - [X_{white\ water}]) \div [X_{headbox}]$$

In the tally of the cycle number, each time the white water returns to the headbox, the cycle number increases by 1. For any species of interest, $C_{i,n}$ gives its concentration in stream i at the n^{th} cycle. For $n > 0$, R represents recycled water. However, for the beginning cycle, in which $n = 0$ and no recycled water is used, R represents additional fresh water or any other water that will be used in place of the recycled water for the later cycles. We use $C_{r,0}$ as the concentration of the species of interest in this water. The beginning cycle is equivalent to a completely open system.

Based on the mass equilibrium, the following equation will be true for any species:

$$H\,C_{h,0} = (F\,C_{f,0} + T\,C_{t,0} + A\,C_{a,0} + R\,C_{r,0}) \quad (1)$$

where $R = D + W + L$ is the total white water recycled in a paper machine.

Therefore, the concentration of Species X in the white water after the beginning cycle is

$$C_{r,1} = H\,C_{h,0}\,(1 - K)/H = (F\,C_{f,0} + T\,C_{t,0} + A\,C_{a,0} + R\,C_{r,0})(1 - K)/H \quad (2)$$

where $H = D + W + L + S + P$.

$C_{f,n}$, $C_{t,n}$, and $C_{a,n}$ are constant for different cycles. If we let $Y = F\,C_{f,n} + T\,C_{t,n} + A\,C_{a,n}$, then

$$C_{r,1} = (Y + R\,C_{r,0})(1 - K)/H \quad (3)$$

where $C_{r,1}$ is the concentration of species of interest in the white water of a zero-recycling system, which means completely open.

For the second cycle,

$$C_{r,2} = (Y + R\,C_{r,1})(1 - K)/H \qquad (4)$$

Combining Eqs. 3 and 4, we obtain

$$C_{r,2} = \frac{Y(1-K)}{H} + R(Y + RC_{r,0})\left(\frac{1-K}{H}\right)^2 \qquad (5)$$

For the third cycle, we get

$$C_{r,3} = \frac{Y(1-K)}{H} + RY\left(\frac{1-K}{H}\right)^2 + R^2(Y + RC_{r,0})\left(\frac{1-K}{H}\right)^3 \qquad (6)$$

R/H is the recycle ratio, and we define it as *r*. Equation 6 can be rewritten as

$$C_{r,3} = \frac{Y(1-K)}{H} + rY\frac{(1-K)^2}{H} + r^2(Y + RC_{r,0})\left[\frac{(1-K)^3}{H}\right] \qquad (7)$$

Rearranging Eq. 7, we have

$$C_{r,3} = Y(1-K)\left[1 + r(1-K) + r^2(1-K)^2\right] \Big/ H + r^3C_{r,0}(1-K)^3 \qquad (8)$$

Similarly, for the fourth cycle, we get

$$C_{r,4} = Y(1-K)\left[1 + r(1-K) + r^2(1-K)^2 + r^3(1-K)^3\right] \Big/ H + r^4C_{r,0}(1-K)^4 \qquad (9)$$

If we extend the calculation to *n* cycles, we get

$$C_{r,4} = Y(1-K)\left[1 + r(1-K) + r^2(1-K)^2 + \ldots + r^{n-1}(1-K)^{n-1}\right] \Big/ H + r^nC_{r,0}(1-K)^n \qquad (10)$$

or

$$C_{r,n} = Y(1-K)\left[\frac{1 - r^n(1-K)^n}{1 - r(1-K)}\right] \Big/ H + r^nC_{r,0}(1-K)^n \qquad (10)$$

Equation 10 can be used to estimate the solids buildup in white water for any cycle at any degree of closure. Because almost every paper mill's water system has already been closed to some extent, it is hard to trace the buildup back to the original zero recycling condition to get the $C_{r,0}$ number. However, this omission should not be a concern. As explained earlier, $C_{r,0}$ can be any water used in the beginning cycle. If we consider the white water currently being reused as $C_{r,0}$ and the current degree of closure as zero, the degree of closure *r* used in Eq. 10 will be the additional degree of closure, or the increased percentage of white water that is expected to be reused. Taking this approach is more convenient for mills because it is also hard to know exactly what the current degree of closure is in most cases.

EQUILIBRIUM CONDITION

At equilibrium, or $r^n = 0$ where *n* is unlimited, Eq. 10 can be simplified as

$$C_{r,eq} = \frac{Y(1-K)}{\left[1 - r(1-K)\right]/H} \qquad (11)$$

`Let $M = T + F + A$, or the total amount of water entering the system from outside sources. Then

$$H = M + R = M/(1 - r) \qquad (12)$$

Equation 12 can be rearranged as

$$C_{r,eq} = \frac{(Y/M)(1-r)}{\left[1/(1-K)\right] - r} \qquad (13)$$

For nonsubstantive species, $K = 0$, then

$$C_{r,eq\text{-}non} = Y/M = (C_f\,F + C_t\,T + C_a\,A)/M \qquad (14)$$

The conclusion we get from Eq. 14 is that, at recycle number *n*, the final equilibrium concentration of nonsubstantive species in a closed water system will be equal to the flow-proportional average concentration of that species in all outside water sources entering the system.

For substantive species, $0 < K <= 1$, then

$$C_{r,eq} < Y/M = C_{r,eq\text{-}non} \qquad (15)$$

Equation 15 indicates that any substantive species will have a final equilibrium concentration less than the flow-proportional average concentration of that species in all outside water sources entering the system. Therefore, it will have a lower equilibrium concentration than it would if it did not adsorb on the fibers.

The conclusion we get from Eqs. 14 and 15 is true no matter what the recycle ratio is. However, the recycle ratio does have an effect on the final equilibrium concentration in that it determines the amount of fresh water coming into the system. If the recycling ratio is higher, then *F/M* will be lower.

Because the concentration of a chemical species of interest in fresh water is normally lower than in thick furnish, the higher the recycle ratio is, the higher will be the final equilibrium concentration. Considering an extreme condition in which no fresh water and no water with additives are involved, the final equilibrium concentration in white water will be equal to that in the thick furnish.

This outcome alleviates the fear that the concentration of some species in white water will rise endlessly and will eventually precipitate out of the water after the water loop is closed. As long as the solid coming into the system is dissolved, it will not precipitate if environment variables such as pH, temperature, charge density, and chemical reactions do not change.

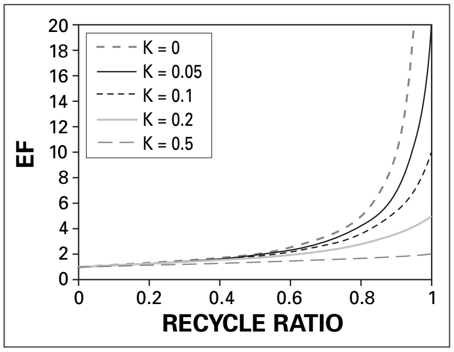
Several articles have raised the question of the possible precipitation of soluble substances from the white water after the wet-end loop is closed [7-9]. From our work, we conclude that increasing the concentration of dissolved materials by recycling white water will not cause precipitation. However, papermaking is a dynamic process. The formation of low-solubility products from unexpected chemical and biological reactions or from changes in pH and temperature may induce a precipitation. Although changes in these parameters are almost ubiquitous in a paper mill, good control of the system will minimize the risk of precipitation.

For those who are used to comparing closed systems to open systems, we can still use the enrichment factor, *EF*, as defined by Alexander and Dobbins.

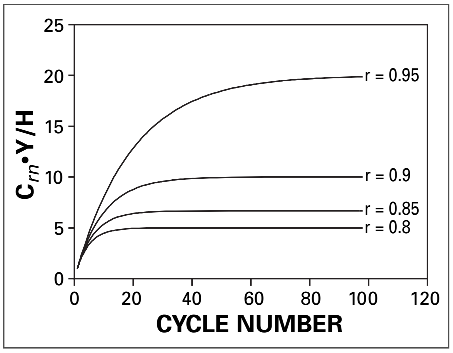
$$EF = C_{r,eq}/C_{r,1} = Y/\left[(Y + R\,C_{r,0})[1 - r + r\,K\right] \qquad (16)$$

If $C_{r,0} = 0$, then

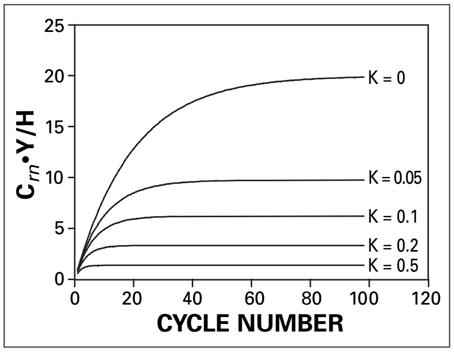
$$EF = 1/(1 - r + r\,K) \qquad (17)$$



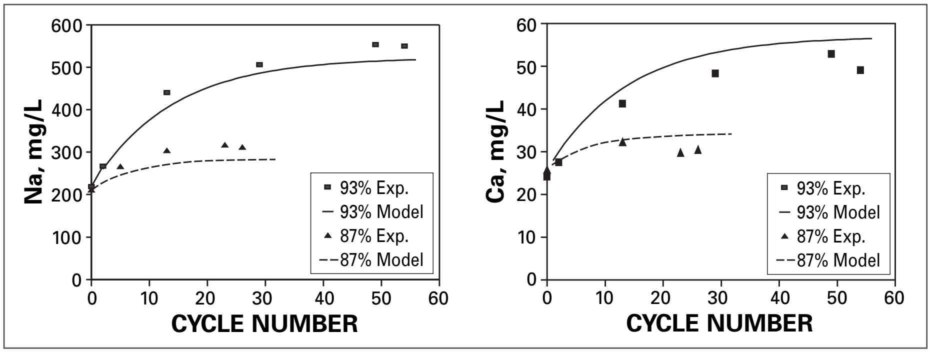
2. Effect of adsorption on the enrichment factor EF.



3. Effect of the recycle ratio on the speed of substance buildup.



4. Effect of adsorption on the speed of substance buildup.



5. Sodium buildup and calcium buildup in white water.

If we further ignore the adsorption, then

$$EF = 1/(1 - r) \qquad (18)$$

This expression is the same as that derived by Alexander and Dobbins.

Figure 2 is a plot of the enrichment factor against the recycle ratio at different adsorption coefficients. Without adsorption, substances in white water build up very fast when the recycle ratio is larger than 80%. At recycle ratios of 95%, 98%, 99%, and 99.9%, the enrichment factor *EF* is 20, 50, 100, and 1000, respectively. Adsorption of dissolved solids on fibers can reduce the buildup dramatically. At a recycle ratio of 99%, the enrichment factor reduces from 100 for no adsorption to 16.8, 9.2, 4.8, and 2.0, respectively, for adsorption coefficients of 0.05, 0.1, 0.2, and 0.5. For a moderate 5% removal of dissolved solid in white water by adsorption, the final equilibrium concentration can be six times lower than without adsorption.

BUILDUP PROCESS

Another question to be answered is, how fast can the white water reach equilibrium? Assuming that $C_{r,0} = 0$, Eq. 10 can be simplified as

$$C_{r,n}\,H/Y = (1-K)\left[\frac{1-r^n(1-K)^n}{1-r(1-K)}\right] \qquad (19)$$

Because *H* and *Y* are constant for a specific mill situation, whenever $(C_{r,n}\,H)/Y$ reaches equilibrium, $C_{r,n}$ will too. Both the recycle ratio and the adsorption coefficient have an effect on the buildup speed.

Figure 3 is a plot of concentration $(C_{r,n}H)/Y$ against cycle number *n* for a simplified situation where adsorption is not considered. The higher the recycle ratio, the longer the time required to reach equilibrium. For recycle ratios of 0.8, 0.85, 0.9, and 0.95, the cycle numbers needed to reach 99% of the final equilibrium concentration are 21, 29, 44, and 90, respectively.

The effect of adsorption on the buildup speed is shown in **Fig. 4**. Generally, the more a substance is removed from the system by adsorption, the smaller the cycle numbers needed for it to reach final equilibrium concentration.

EXPERIMENTAL VERIFICATION

We conducted a laboratory study to verify the model, simulating two degrees of closure, 93% and 87%. The degree of closure is equivalent to the recycle ratio defined in the model—that is, the percentage of recycled white water in the total headbox furnish.

Changes in the concentration of sodium and calcium were monitored, and the results are given in **Fig. 5**. Predicted sodium and calcium buildups from the model for $K = 0$ are also given in the figures for comparison. Measured values for both the sodium and calcium buildup agree fairly well with the model predictions. The prediction of sodium buildup is slightly lower than that measured, and that of calcium is slightly higher, which means the adsorption constant *K* is different for Na^+ and Ca^{2+}. We did not measure the adsorption constants of Ca^{2+} and Na^+ on this thick-stock furnish in this study.

CONCLUSIONS

Mathematical models based on mass equilibration can predict the buildup of nonsubstantive substances in closed white water systems. These models validate the steady-state value and the length of time necessary to achieve steady state.

According to the model, the final equilibrium concentration of any dissolved solids in a closed water system will be less than or equal to the flow-proportional average concentration of that species in all outside water sources entering the system. The solids coming into the system in dissolved form will not precipitate out of the water solely because of the concentration increase, no matter how many times they are recycled and no matter what the degree of closure is.

The final equilibrium concentration of solids of interest depends on the degree of closure and the degree of adsorption. For dissolved solids coming with the thick stock, the higher the recycle ratio is, the higher will be the final equilibrium concentration.

Moderate removal of a solid from the system by adsorption can dramatically reduce the equilibrium concentration of the solid. The degree of closure and the degree of removal adsorption also determine the speed at which the solid reaches equilibrium concentration during closure. The higher the degree of closure and the lower the degree of removal, the longer it takes to reach equilibrium.

Experimental results from simulated laboratory closure agreed nicely with the model prediction. **TJ**

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INSIGHTS FROM THE AUTHORS

Understanding the fundamentals of contaminant buildup in a paper machine is the key to reducing the fresh water consumption. That is why we chose this particular topic for our research. Papermakers and researchers have known that the closing of the water system will increase the contamination level in a paper machine, but it has not been known how high and how fast the buildup will be. This paper provides a simple model to answer these questions.

To be effective, the model must include all water streams in a paper machine, which is too complicated for analysis. We simplified the streams by making some reasonable assumptions.

The most interesting part of the research is that the contaminants cannot precipitate out by merely increasing the degree of closure. The next step in the research would be collecting mill data to confirm the model.

I believe that papermakers can best use the information presented to predict how high a water closure level can be reached in their mills. Using this level as a target, they can optimize their operating conditions.

Xu

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