Effects of recycling peroxide liquor on brightness of mechanical pulp

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ABSTRACT: The high cost of bleaching softwood mechanical pulps to 80% brightness with peroxide can be partly offset by recycling the unreacted peroxide in the effluent. However, the situation is complicated by the presence of dissolved organic material, "aged" silicate, and calcium extracted from the pulp. This study examines the effects of these materials on brightening efficiency. Dissolved organic material did not consume peroxide in subsequent cycles. "Aged" silicate stabilized peroxide as efficiently as fresh silicate. Interaction of silicate with calcium and magnesium caused silicon residue to precipitate on the fibers, with deposition increasing with the number of cycles. Calcium silicate adhered strongly to stainless steel, while magnesium silicate did not.

KEYWORDS: Bleaching, brightening, effluents, mechanical pulps, peroxides, recycling.

A one-stage peroxide treatment is traditionally used to brighten softwood mechanical pulp to a moderate brightness level of 70% Elrepho. With the introduction of high-yield pulps in fine paper grades, 80% brightness is required. To achieve this greater brightness, it is necessary to use higher peroxide concentrations and pulp consistencies. When pulp is brightened under these conditions, a large fraction of the peroxide remains unreacted. At a high peroxide charge, maximum brightness is obtained while consuming only 50–75% of the oxidant *(1)*. Given the relatively high cost of peroxide, it is imperative to reuse the residual chemical.

Most of the mills that use peroxide to produce high-yield pulp at 80% brightness employ some type of bleach-liquor recycle, be it a one- or two-stage process. In the one-stage process, the initial peroxide application is high (4–6% on pulp). The effluent, containing a significant amount of unreacted peroxide, is recycled to the beginning of the brightening stage together with fresh peroxide, sodium silicate, and alkali.

Some mills are using a two-stage process in which the pulp is brightened with two peroxide stages, with each stage having a lower charge than the one-stage process. The majority of the fresh peroxide is added to the second stage to achieve the target brightness. The residual liquor from this stage, which contains a high concentration of unreacted peroxide, is recycled to the first stage, where the pulp is pre-brightened under milder conditions *(1)*.

Many researchers have shown the advantages of recycling spent liquor to utilize the unreacted peroxide *(1–4)*. However, there has not been much research into the effects of recycling the other components in the spent liquor. The recycled effluent contains residual peroxide as well as dissolved organic material, sodium silicate, magnesium sulfate, and metals. In a preliminary study on brightening of Norway spruce thermomechanical pulp (TMP) with recycled filtrate, it was found that:

- The dissolved organic material in the filtrate increased significantly with each successive cycle.
- After the first cycle, the peroxide-brightened pulp contained more silicon and less calcium and magnesium than the original DTPA (diethylenetriamine pentaacetic acid)-pretreated pulp.
- The calcium and magnesium contents of the brightened pulp increased with each successive cycle.

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- The quantity of transition metals (Fe, Cu, and Mn) in the pulp and filtrate did not change appreciably with continued filtrate recycling.

The research presented here is an extension of the aforementioned exploratory study. The objective of the current research was to determine the effects of the dissolved organics, silicate, and metals on brightening when peroxide liquor is recycled.

Experimental

Pretreatment

Norway spruce TMP made in-house and a commercial chemithermomechanical pulp (CTMP) were examined in this study. Pulp samples were pretreated using either or both of the following conditions.

- DTPA chelated—0.4% DTPA, 3% consistency, pH 5.5–6.0, 90°C, 0.5 h.
- Superchelated—Washed three times with 0.1*M* HCl at 3% consistency, 0.5 h, room temp.; washed with distilled water to pH 4.5, chelated with 0.4% DTPA at 3% consistency, 0.5 h, 90°C.

Peroxide brightening

Starting with a pulp partially dried to approximately 50% consistency, peroxide brightening was conducted in plastic bags at 15% consistency with varying concentrations of hydrogen peroxide, sodium silicate (41 Bé, 28.7% SiO_2), and sodium hydroxide. Magnesium sulfate was added at 0.05% based on pulp. The bags were submerged in a water bath at 60°C. After 3 h, the spent liquor was squeezed from the pulp and retained. The pH was adjusted to 5.5 with sodium bisulfite then the pulp was filtered and washed.

The spent liquor was analyzed for total organic carbon (TOC), silicon, magnesium, calcium, iron, manganese, and copper. A Beckman 915 analyzer was used to measure TOC. Metal ions were measured with a Spectro inductively coupled plasma emission spectrometer.

I. Characteristics of spent liquors from first peroxide stage[a]

Sample no.	Pulp	Pretreatment	H_2O_2, % Initial	H_2O_2, % Residual	TOC conc. in liquor, ppm
1	Spruce TMP	DTPA	3.0	0.42	3437
2	Spruce TMP	Superchelated	3.0	0.42	3499
3	Spruce CTMP	Superchelated	3.0	0.52	2696
4	Spruce TMP	DTPA	1.0	0.22	1100
5	Spruce CTMP	DTPA	10.0	0.77	2050
6	Spruce CTMP	DTPA	3.0	0.07	1955
7	Spruce CTMP	DTPA	4.0	1.18[b]	1900
8[c]	Spruce/fir CTMP	DTPA	10.0	...	2700
9[c]	Spruce TMP	DTPA	10.0	...	...

[a]Brightening conditions: 3% NaOH, 15% consistency, 60°C, 3 h
[b]4% sodium silicate and 0.05% $MgSO_4 \cdot 7H_2O$ included in brightening liquor
[c]Effluent stored at room temperature for 48 h prior to reacting with H_2O_2; all other samples refrigerated prior to use.

II. Reaction of peroxide spent liquors with fresh peroxide under pulp brightening conditions[a]

Sample no.[b]	H_2O_2 applied, %	H_2O_2 residual, % of applied
1–3	3.0	>92
4	1.0	99
5	10.0	97
6	3.0	98
7	4.0	98
8[c]	10.0	65
9[c]	10.0	61

[a]Conditions: 3% NaOH, 0.05% $MgSO_4 \cdot 7H_2O$, 4% silicate (equal to amounts added if pulp was present at 15% consistency), 60°C, 3 h
[b]Liquor:distilled water = 4:1 (v/v)
[c]Stored at room temperature for three days; all other samples stored under refrigeration

III. Comparison of fresh and aged silicate in the brightening of spruce TMP

Silicate	pH Initial	pH Final	H_2O_2 consumed, %[a]	Elrepho brightness, %[b]
Aged	11.0	9.6	56.5	72.7
	11.0	9.3	53.1	72.3
Fresh	11.0	9.5	56.3	72.4
	11.0	9.0	56.9	71.6

[a]Conditions: 2.5% H_2O_2, 2.5% NaOH, 2% silicate, and 0.05% $MgSO_4 \cdot 7H_2O$ on pulp, 15% consistency, 60°C, 3h, silicate concentration 3.5 g/L
[b]Unbleached brightness 59.4%

IV. Comparison of results for peroxide brightening of TMP in the presence of 100% fresh silicate or 100% recycled silicate

	Fresh silicate [a]	*Recycled silicate* [b]
pH		
Initial	11.2	11.15
Final	9.5	9.0
Peroxide		
Initial, %	2.5	2.5
Residual, %	0.98	0.89
Elrepho brightness, %	72.7	72.1

[a]Conditions: 2.5% NaOH, 0.05% $MgSO_4 \cdot 7H_2O$, 15% consistency, 60°C, 3h
[b]Initial filtrate was obtained after brightening TMP with peroxide under stated conditions plus 5% silicate application. For brightening with recycled filtrate, silicate application was 3%.

Peroxide brightening with spent liquor

The method for peroxide brightening with spent liquor was the same as that used with fresh liquor. In this case, though, 60% of the solution used to brighten the pulp was recycled liquor from the preceding brightening stage. Fresh makeup peroxide and alkali were added to achieve the correct brightening concentrations, taking into account the concentrations of residual chemicals in the recycled liquor. However, the amount of fresh silicon (in the form of silicate) added to the liquor was 55% rather than 40% of the amount present in the initial cycle. This standard estimated correction was made to account for the silicon retained by the brightened pulp.

Peroxide reactions in the absence of pulp

Spent liquor was reacted with fresh peroxide in the absence of pulp in polyethylene bottles submerged in a water bath at 60°C. The spent liquor and silicate solutions were first preheated in the water bath and pH was adjusted to 11.2. At the predetermined temperature, fresh peroxide was added. An aliquot was removed every 30 min, and peroxide consumption was measured.

Silicate, calcium, and magnesium deposition on stainless-steel screen

Sodium silicate solutions were prepared in concentrations typical for a peroxide bleaching stage (38 mmoles SiO_2/L). The solutions were heated to 60°C in a water bath. Stainless-steel screens (30 mesh, wire diameter 0.28 mm, hole opening 0.57 mm, 2 in. x 2.5 in.) were suspended in each solution with a stainless steel wire. The desired amount of either calcium or magnesium ions were then added to the silicate solutions. The capped mixtures were stirred vigorously with a magnetic stirring bar while the temperature was maintained at 60°C. The pH was kept constant by adding small amounts of 1*N* NaOH as needed. After 48 h, the screens were withdrawn from the solutions, and any loosely attached gel was shaken off. After air drying, the weight increase of the screen was measured to determine the amount of scale formation. Electron microscopy was conducted on the screens at low magnification to characterize any scale deposition on the surface.

Results and discussion

Consumption of peroxide by organic material in filtrate

Samples of TMP and CTMP, previously pretreated with DTPA alone or superchelated with HCl followed by DTPA, were brightened with H_2O_2. Filtrates from these treatments were collected and TOC contents determined. Results are presented in **Table I.**

The liquors were subsequently reacted with fresh peroxide in the absence of pulp and in the presence of silicate and magnesium sulfate under typical brightening conditions. Peroxide consumption in these tests is shown in **Table II.** The spent liquors that had been refrigerated while awaiting use (Samples 1–7) consumed essentially no peroxide. Moreover, the residual peroxide in the refrigerated samples did not decrease upon storage. On the other hand, Samples 8 and 9, which had been stored at room temperature for three days, consumed significant amounts of peroxide both during storage and in subsequent reaction under brightening conditions.

These latter findings are in agreement with results obtained in the exploratory study performed earlier. The reason for the storage-temperature effect on peroxide consumption was not investigated. However, these findings suggest that if the spent liquor is recycled without prolonged storage, the recycled organic material present will not consume peroxide during subsequent brightening stages.

Inactivation of silicate during peroxide brightening

Another factor potentially capable of affecting the brightening efficiency of recycled peroxide filtrate is the state and condition of the silicate contained in the spent liquor. Conceivably, the polymer structure of the silicate *(5)* could be modified during the brightening process such that it becomes inactivated and, hence, unable to stabilize the peroxide against decomposition when recycled. To test this proposition, a silicate solution (6 g/L) was heated (i.e., "aged") for 9h at 60°C in the absence of pulp and brightening chemicals (pH 10.5). Spruce TMP was brightened with peroxide liquor containing "aged" silicate in one case and fresh silicate in the other. The results, compiled in **Table III**, show that the heating of aqueous sodium silicate at 60°C had no significant effect on brightening or peroxide consumption.

In related experiments, spruce TMP was brightened with peroxide using liquor in which the added silicate was 100% recycled. The results of this test were compared with those obtained in an otherwise similar experiment in which 100% fresh silicate was included in the liquor. As seen in **Table IV**, there was no significant difference in peroxide consumption or brightness when TMP was brightened with 100% recycled or with 100% fresh silicate.

Effect of calcium and magnesium in recycled filtrate

A preliminary study revealed that portions of the calcium and magnesium initially present in Norway spruce TMP desorbed during peroxide brightening. Since calcium and magnesium have similar chemical properties, a logical area of inquiry was to determine whether the liberated calcium has a stabilizing effect on peroxide during brightening, as does magnesium when added in the form of $MgSO_4 \cdot 7H_2O$.

Norway spruce TMP was pretreated with DTPA alone or superchelated (HCl followed by DTPA) in an attempt to produce a pulp essentially free of calcium and magnesium. The metal contents of the pulps are reported in **Table V**. The results indicate that DTPA alone was ineffective in removing calcium and magnesium from the pulp. This situation was improved considerably by pretreating the pulp consecutively with dilute HCl and then with DTPA. This superchelated pulp was used in most experiments where an essentially calcium- and magnesium-free pulp was required. The increase in silicon is attributed to contamination by the Na_5DTPA (alkaline solution in a glass bottle).

V. Effect of DTPA and hydrochloric acid pretreatments on the metal content of spruce TMP

	Metal content, ppm*					
Pretreatment	*Ca*	*Mg*	*Si*	*Fe*	*Cu*	*Mn*
None	1058	88	11	47	4	118
DTPA chelated	948	78	19	45	2.5	1
Superchelated	34	6	14.5	34	3.5	< 1

*Based on pulp

Peroxide brightening of superchelated TMP with systems containing added calcium and magnesium salts

The effect of magnesium and calcium on the brightening of superchelated Norway spruce TMP was investigated. Magnesium sulfate and calcium nitrate were added to the brightening system at silicate applications of 2% and 4%. The results for peroxide consumption and brightness are illustrated in **Figs. 1 and 2**, respectively.

As seen in Fig. 1, peroxide consumption was generally lower in the presence of magnesium than in the presence of calcium, the exception being the case where low amounts of calcium were added at the higher silicate application. Differences in the effects of the two metals on peroxide consumption were relatively small at concentration levels typical of those found in DTPA-treated TMP (<25 mmoles/kg of pulp). There was a minimum in peroxide consumption with calcium application of 25–50 mmoles/kg of pulp, whereas increasing addition of magnesium caused only a parallel decrease in peroxide consumption. Peroxide consumption was lower for both calcium and magnesium at all addition levels when 4% silicate was added compared with 2%.

Figure 2 shows that at relatively low levels (0–100 mmoles/kg of pulp) of calcium and magnesium addition, each metal had a small but significant beneficial effect on the brightness of the TMP. Further addition of magnesium had little additional beneficial effect on brightness, while increasing calcium addition had the effect of markedly decreasing brightness. This brightness decrease was less severe in the instance where 4% silicate was present in the brightening system.

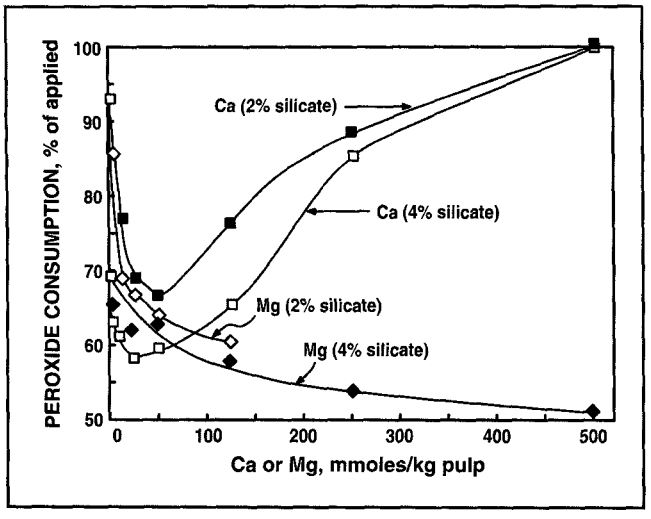
One hypothesis to explain the adverse effect of high concentrations of calcium is that the reagent-grade calcium nitrate contaminated the reaction solution with transition metals. This hypothesis was rejected based on the trace-metal content of a concentrated $Ca(NO_3)_2$ solution (10,000 ppm Ca). It is possible that silicate interacted with calcium, at high concentrations, in a manner that deactivated the silicate as a trap for transition metals. Such an interaction would be contrary to silicate interaction with high concentrations of magnesium. Other differences in the interaction of silicate with calcium and magnesium are described later in this report.

Collectively, these results indicate that, in the concentration ranges typical of those found in the DTPA-pretreated pulp and at a 4% silicate application level, calcium has a similar and possibly a marginally more favorable effect on peroxide consumption and brightness than does magnesium. In practice, this means that—to the extent that calcium in the pulp and recycled filtrate is available to function as a peroxide stabilizing agent—it can reinforce or supplement the effect of magnesium without adversely affecting final brightness.

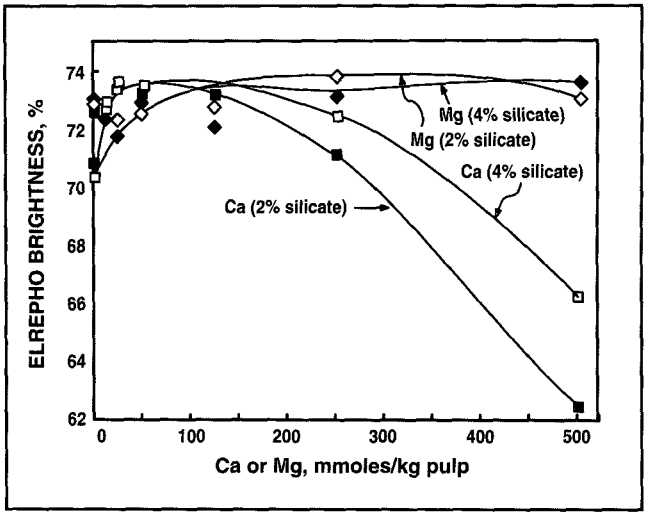
Calcium, magnesium, and silicon interactions

The filtrates from the brightening experiments described in the preceding section were collected and analyzed for calcium, magnesium, and silicon. The results, presented in **Tables VI**

1. Effect of calcium and magnesium addition on peroxide consumption in the brightening of demineralized spruce TMP. Brightening conditions: 2.5% H_2O_2, pH 11.2, 15% consistency, 60°C, 3 h.



2. Effect of calcium and magnesium addition on brightness in the brightening of demineralized spruce TMP. Brightening conditions: same as Fig. 1.



VI. Calcium and silicon in filtrate after peroxide brightening of demineralized spruce TMP in the presence of added calcium nitrate

Calcium, ppm[a]		Silicon in filtrate, ppm[a]
Added	In filtrate	
0	5 ...[b]	6,090
100	16 (16)	6,294
300	34 (11)	6,180
1,000	153 (15)	5,074
2,000	164 (8)	3,090
5,000	357 (7)	1,284
10,000	1213 (12)	1,072
20,000	5444 (27)	391

[a]Based on pulp
[b]Percent recovery

VII. Magnesium and silicon in filtrate after peroxide brightening of demineralized spruce TMP in the presence of added magnesium sulfate

Magnesium, ppm[a]		Silicon in filtrate, ppm[a]
Added	In filtrate	
0	10 ..[b]	6,090
60	30 (50)	6,010
300	149 (50)	5,755
600	283 (47)	5,273
1,200	459 (38)	3,629
3,000	269 (9)	1,210
6,000	286 (5)	88
12,000	471 (4)	24

[a]Based on pulp
[b]Percent recovery

and VII, indicate that a very high percentage of these elements was retained by the pulp and that generally the percentage retained increased with increasing amounts of the metal added to the brightening system. The acidic groups in wood pulps are excellent at exchanging monovalent cations for divalent cations, particularly Ca^{2+} *(6)*. Large amounts of silicon were retained by the pulp, particularly in the case where a high initial magnesium concentration was present. This latter finding is compatible with the known lower solubility of $MgSiO_3$ compared with that of $CaSiO_3$.

Peroxide brightening of spruce TMP using recycled filtrate

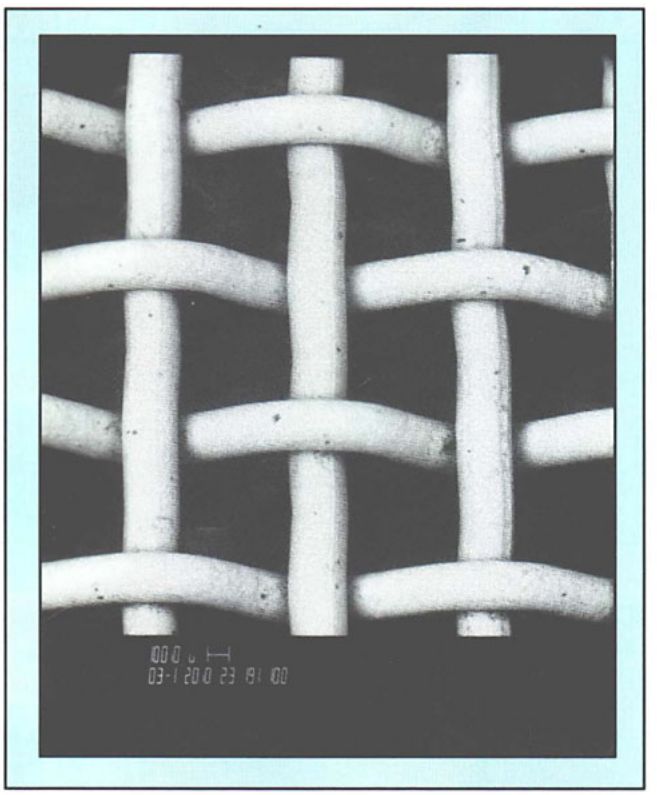
Based on the research reported so far, the only concern about effluent recycling appears to be the deposition of siliceous material on the pulp. Such deposition is accelerated by high concentrations of calcium and magnesium (Tables VI and VII). Consequently, the next phase of the research focused on two issues:

1. Determine whether there was a buildup of calcium and magnesium in the filtrate with recycling (calcium desorption from pulp and $MgSO_4 \cdot 7H_2O$ addition).
2. If there was a buildup, determine whether there was a critical concentration that triggered silicate precipitation.

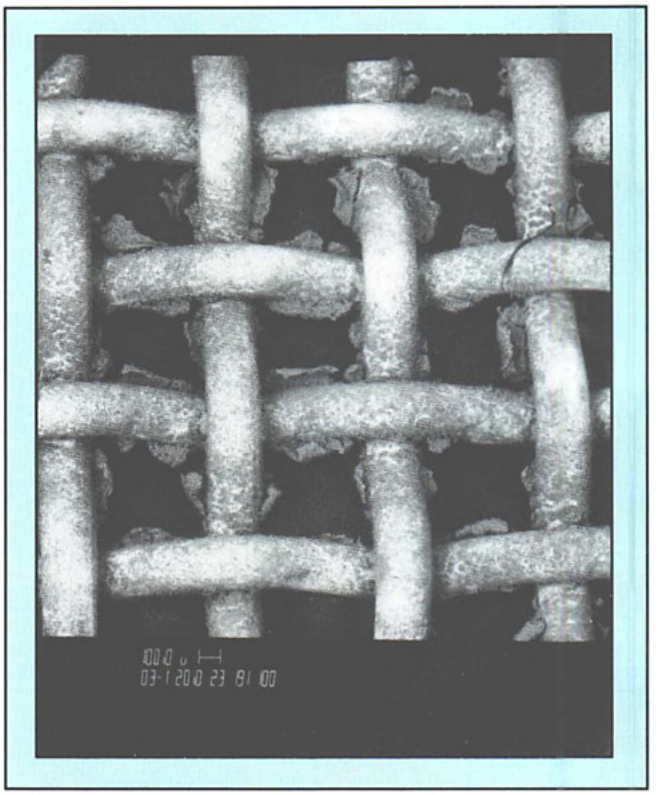
The DTPA-pretreated pulp was brightened, and 60% of the effluent was collected and used to brighten a fresh batch of pulp. This procedure was continued for four cycles. In each stage, some of the silicon precipitated on the pulp and was strongly held. The percentage of applied silicon that was strongly held by the pulp showed an overall increase with increasing recycling, as seen in **Table VIII**.

It can be seen that, from cycle to cycle, there were significant variations in the initial silicon charge (e.g., DTPA-pretreated—1). These variations were due to silicon addition in Cycles 2–4 based on an estimated silicon concentration in the liquor from the previous stage. Also, the amount of silicon that was strongly and weakly bound to the pulp varied significantly from cycle to cycle. The experiment was repeated with DTPA-pretreated pulp (DTPA-pretreated—2), but we were unable to eliminate the variations in initial silicate concentration. However, we did reduce the range from 989 ppm (4931–5920 ppm) to 726 ppm (4868–5594 ppm) silicon on pulp. In the first trial, three cycles were completed before there was high silicate deposition (14.6% of

3. Photomicrograph (20X) of scale deposition on stainless-steel screen (Sample 6 in Table XII)



4. Photomicrograph (20X) of scale deposition on stainless-steel screen (Sample 16 in Table XII)



applied silicon). In the repeat experiment, 15.9% of the applied silicon deposited in the second cycle.

When the superchelated pulp with low calcium and magnesium concentrations was used, five and four cycles (duplicate trials) were required before large amounts of the silicon precipitated, as seen in Table VIII. Therefore, it appears that calcium and magnesium were associated with silicate precipitation.

The mass balances for silicon, calcium, magnesium, and the transition metals are presented in **Table IX** for four cycles using one of the DTPA-pretreated pulps (DTPA—2 in Table VIII). It can be seen that with the exception of silicon in Cycle 3, the mass balances are quite accurate. The partitioning of the elements between pulp and effluent is presented in **Table X**.

It can be seen in Table X that the total recovered silicon is less than indicated by the data in Table IX, while the totals for the metals are approximately equal. In Table IX, the filtrate was pressed from the pulp and analyzed with the unwashed pulp. The well-washed pulp in Table X was analyzed, and the reported silicon contents represent strongly held siliceous materials. The differences in silicon content represent weakly bound siliceous material that apparently was washed out without any associated calcium or magnesium. As discussed previously, the acidic groups in wood pulps readily exchange monovalent cations for divalent cations *(6)* and probably exchanged Na^+ for Ca^{2+} (from the silicate) during the washing process.

It appears that the magnesium was associated with the strongly bound silicates. As seen in Table X, there was essentially no magnesium in the effluent of Cycles 2–4, even though 0.05% $MgSO_4 \cdot 7H_2O$ (≈ 50 ppm Mg) on pulp was added on each occasion. Most of the magnesium remained in the effluent from the first cycle, and silicate precipitation was minimal. A dramatic increase in both silicate and magnesium precipitation was observed during the second cycle. However, it is difficult to assess the interaction between strongly bound silicate and calcium because of the high calcium concentration in both phases.

Based on the four experiments reported in Table VIII, no unique concentration of calcium, magnesium, or total of the two triggered precipitation. However, a dramatic increase in precipitation occurred simultaneously for silicates and magnesium on all occasions. This indicates that interactions between silicate and magnesium, and most likely calcium as well, lead to precipitation. However, the process is obviously sensitive to variables other than the concentration of alkaline earth metal.

The brightness and H_2O_2 consumption data for the four trials described in Table VIII are summarized in **Table XI**. Generally, the first cycle consumed slightly less H_2O_2 than the later cycles. There were no significant variations in bleached brightnesses.

VIII. Effect of filtrate recycling on silicon deposition on spruce TMP during peroxide brightening

Cycle	Silicon, ppm[a] Fresh	Recycled	Total	Silicon on TMP after brightening, % of applied
		DTPA-pretreated—1		
1	5920	0	5920	2.5
2	2368	3207	5575	7.6
3	2812	2119	4931	14.6
4	2960	2045	5005	11.6
		DTPA-pretreated—2		
1	5000	0	5000	7.5
2	2750	2844	5594	15.9
3	2750	2118	4868	14.2
4	2750	2415	5165	14.6
		Superchelated—1		
1	6000	0	6000	5.5
2	2400	3378	5778	3.5
3	3300	3572	6872	3.6
4	3300	4762	8062	7.1
5	3300	4388	7688	10.3
6	3300	3912	7212	13.8
		Superchelated—2		
1	5236	0	5236	0.7
2	2855	3077	5932	0.8
3	2855	4150	7005	0.7
4	2855	4627	7482	16.7

[a]Based on pulp

IX. Recovery of silicon, calcium, magnesium, and transition metals in the brightening of DTPA-pretreated spruce TMP with recycled peroxide filtrate[a]

Cycle No.		Metal content, ppm[b] Si	Ca	Mg	Fe	Cu	Mn
1	Added	5000	948	128	45	3.4	1.0
	Recovered	5213	949	120	49	4.7	0.9
2	Added	5594	1103	156	46	3.7	1.1
	Recovered	5468	1172	160	47	4.9	1.3
3	Added	4868	1209	132	45	3.7	1.0
	Recovered	5628	1204	124	47	4.1	0.7
4	Added	5165	1184	128	45	3.8	1.0
	Recovered	5403	1176	121	49	4.5	0.7

[a]Brightening conditions: 4% H_2O_2, 4% NaOH, 4% silicate, 0.05% $MgSO_4 \cdot 7H_2O$, 15% consistency, 60°C, 3 h
[b]Based on pulp

Effect of calcium and magnesium on silicate deposition

Silicon scale buildup in process tanks and pipes in a peroxide bleaching operation also may be attributed to the interaction of calcium and magnesium (hard water) with the sodium silicate. To investigate this possibility, magnesium and calcium ions were added to sodium silicate solutions at a concentration typical for peroxide brightening (described in the Experimental section), and pieces of stainless steel screens were immersed in these solutions. The stainless-steel screen provided a large surface area for the potential deposition of silicate. The weight difference of the screen indicated the amount of scale deposited. Sample results are reported in **Table XII**. The term "precipitate" in Table XII refers to material that was collected by centrifuging and filtering of the solution, and scale is the material adhering to the metal screen. The amount of scale was regarded as insignificant when less than 2.0 mg.

These experiments were repeated several times with the screen grounded and ungrounded. There was some variability in the amount of deposit. However, there was one constant trend in all experiments, i.e., calcium silicates adhered to the stainless steel while magnesium silicates did not. The effect of calcium (Table XII) clearly demonstrates that silicate scale formed only when precipitation occurred, which suggests that the silicate particles must become destabilized (precipitated) before they deposit on the metal surface. The first sign of scaling was at about 50 ppm calcium (1.2 m*M*), which is normal for some groundwater. **Figures 3 and 4** are electron micrographs of screen samples 6 and 16 (Table XII) showing the scale caused by calcium and magnesium, respectively.

For the system containing magnesium, very little scaling occurred, even when a large amount of silicon-containing material precipitated. This suggests that the magnesium silicate precipitate has a far lower affinity for the metal surface than the calcium silicate material.

Future work

Three important observations suggest that calcium and magnesium react uniquely with sodium silicate.

1. In the presence of high concentrations of calcium, sodium silicate was unable to stabilize H_2O_2 brightening liquor. The opposite was true with high concentrations of magnesium (Fig. 1).
2. Upon continued filtrate recycling, the magnesium initially present in the bleaching liquor was totally deposited on the pulp, but calcium

had a greater tendency to stay in solution when bleaching filtrate was recycled (Table X).

3. Calcium silicate precipitate adhered to stainless steel, while the magnesium silicate did not (Table XII).

Based on these observations, we have begun studying the mechanism by which calcium and magnesium interact with sodium silicate under peroxide brightening conditions. The results of this research will be presented in a future report.

Conclusions

The economics of brightening softwood mechanical pulps to brightnesses in the range of 80% Elrepho dictate that recycling of the residual peroxide be considered. However, together with the unreacted peroxide, the recycled effluent contains dissolved organic material, "aged" silicate, and calcium and transition metals extracted from the pulp.

In a series of experiments aimed at identifying and assessing the effects of these variables, the following results were obtained.

- Organic material in the recycled liquor did not significantly contribute to peroxide consumption if the filtrate is recycled quickly or is stored at 5°C between cycles. Also, the recycled silicate is as effective as fresh silicate in stabilizing the peroxide.
- The small amount of calcium extracted from a DTPA-chelated pulp had an advantageous effect on peroxide stability and brightness. Under these same conditions, transition metals were not extracted to any significant extent.
- Silicon-containing residues were deposited on the TMP when fresh peroxide liquor was used to brighten it. Furthermore, the deposition increased significantly upon using recycled filtrate. The deposition appears to be at least associated with the presence of added

X. Distribution of silicon, magnesium, calcium, and transition metals between pulp and filtrate in the brightening of DTPA-pretreated spruce TMP with recycled peroxide filtrate[a]

	Metal concentration, ppm[b]					
	Si	*Ca*	*Mg*	*Fe*	*Cu*	*Mn*
Original TMP	14	1058	88	47	4	118
DTPA-chelated TMP	17	948	78	45	2.5	1.0
Peroxide-brightened TMP						
1st cycle						
Pulp	376	690	74	45	4.5	<1
Filtrate	4791	259	46	1.7	0.4	<1
Total	5167	949	120	47	4.9	...
2nd cycle						
Pulp	955	737	153	46	4.5	<1
Filtrate	3600	435	7	0.6	0.4	<0.01
Total	4555	1172	160	47	4.9	...
3rd cycle						
Pulp	690	810	123	45	3.7	<1
Filtrate	4025	394	1	0.6	0.6	<0.01
Total	4715	1204	124	46	4.3	...
4th cycle						
Pulp	753	804	120	47	4.0	<1
Filtrate	4000	372	1	0.4	0.5	<0.01
Total	4753	1176	121	47	4.5	...

[a]Brightening conditions: same as Table IX
[b]Based on pulp

XI. Peroxide consumption and brightness of spruce TMP brightened with recycled filtrate*

Pulp	*H_2O_2 residual, % of applied*	*Elrepho brightness, %*
Unbrightened pulp		
Original	—	59.0
DTPA-pretreated	—	59.4
Superchelated	—	58.1
Brightened pulp		
DTPA-pretreated—1		
Cycle 1	41.7	75.5
Cycles 2–4	38.6 ± 3.0	75.4 ± 0.2
DTPA-pretreated—2		
Cycle 1	42.5	75.4
Cycles 2–4	37.9 ± 2.0	75.4 ± 0.2
Superchelated—1		
Cycle 1	42.9	75.3
Cycles 2–6	32.6 ± 3.0	76.2 ± 0.2
Superchelated—2		
Cycle 1	47.5	74.9
Cycles 2–4	40.8 ± 0.9	75.2 ± 0.3

*Brightening conditions: 4% H_2O_2, 4% NaOH, 4% silicate, 0.05% $MgSO_4 \cdot 7H_2O$, 15% consistency, 60°C, 3 h

XII. Deposition of silicon-containing scale on ungrounded stainless-steel screen under peroxide brightening conditions in the presence of variable concentrations of calcium and magnesium*

Sample No.	*Metal conc., mM*	*Weight of scale, mg*	*Precipitate formed*
		Calcium	
1	0.00	0.6	No
2	0.40	1.1	No
3	0.80	1.8	No
4	1.20	6.2	Yes
5	1.35	5.5	Yes
6	1.50	37.4	Yes
7	1.65	19.8	Yes
8	1.80	4.7	Yes
		Magnesium	
9	0.00	0.7	No
10	1.00	0.6	No
11	1.60	0.4	No
12	1.80	1.1	Yes
13	2.00	1.0	Yes
14	2.40	0.9	Yes
15	2.90	1.2	Yes
16	3.50	0.9	Yes

*Conditions: 38.0m*M* SiO_2, pH 9.2, 60°C, 48 h, 30-mesh 301 stainless-steel screen

magnesium (Epsom salt) and calcium extracted from the pulp.

- Precipitate from the interaction of calcium and silicate adhered to a stainless-steel screen, while the magnesium silicate precipitate did not. ◼

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