Oxidative extraction of hardwood and softwood kraft pulps with sodium carbonate–sodium hydroxide mixtures or oxidized white liquor during multistage bleaching

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ABSTRACT

A variety of synthetic and mill liquors—sodium carbonate, kraft white liquor, oxidized white liquor, and soda white and green liquors—were evaluated as replacements for sodium hydroxide during oxidative extraction (EO and EOP) of hardwood and softwood pulps. These alkalis were screened based on the rate of decomposition of hydrogen peroxide, which was significant in synthetic kraft white liquor and in all mill liquors. Kraft white liquor is unsuitable for oxidative extraction because sodium sulfide rapidly decomposes hydrogen peroxide. The soda-mill liquors contained transition metals that hastened peroxide decomposition. Removal of transition metals is an option, and magnesium salt was a better scavenger than DTPA. Peroxide decomposition in the other synthetic liquors was negligible. Pulps extracted with 100% sodium carbonate required excessive chlorine dioxide to achieve acceptable brightness (86–87% ISO). The study concludes that mixtures of sodium carbonate and sodium hydroxide (50/50 or 40/60) or synthetic oxidized white liquor are effective substitutes for caustic soda in oxidative extraction.

Application: *Caustic soda is a by-product of chlorine production, so its cost is expected to increase as pulp mills phase out their use of chlorine. This study evaluates alternatives to caustic soda for oxidative extraction of pulps during multistage bleaching.*

SODIUM HYDROXIDE IS WIDELY USED in alkaline and oxidative extraction (E, EO, EP, or EOP) of pulps. (See **Table I** for list of abbreviations used in this article.) With the elimination of chlorine from pulp bleaching, the price of caustic is likely to increase, and pulp mills may need to use other alkalis in extraction of pulps.

Oxidized white liquor (OWL) is being used in oxygen delignification (O) and alkaline extraction (E) of pulp *(1–3)*. However, its use in oxidative extraction (EO, EP, or EOP) is yet to be explored. Sodium carbonate was proposed as an alkali for extraction of nonwood pulps *(4–6)*. Under equivalent application, sodium carbonate-extracted pulps have higher CE permanganate (P) number than sodium hydroxide-extracted pulps *(3)*, requiring more chlorine dioxide charge in final D stage(s) to reach equivalent pulp brightness *(7)*.

There is little impediment to using OWL for EO extraction of pulps. However, its use in EP and EOP extraction is questionable because the sulfur compounds in OWL can initiate decomposition of hydrogen peroxide, restricting its availability to decrease CE P number and increase pulp brightness. Soda white liquors (SWL) and green liquors (SGL) are sulfur-free alkalis, containing mainly sodium hydroxide and sodium carbonate. Their use in EP or EOP extraction of pulps depends on the concentration of transition metals that initiate the decomposition of hydrogen peroxide, leading to the formation of hydroxy radicals *(8)*. Hydroxy radicals are powerful nonselective oxidants that degrade cellulose and reduce pulp strength. Hydroxy radicals also decrease the concentration of hydroperoxy radicals and anions, which are important for delignification and brightening of pulps, respectively *(8)*.

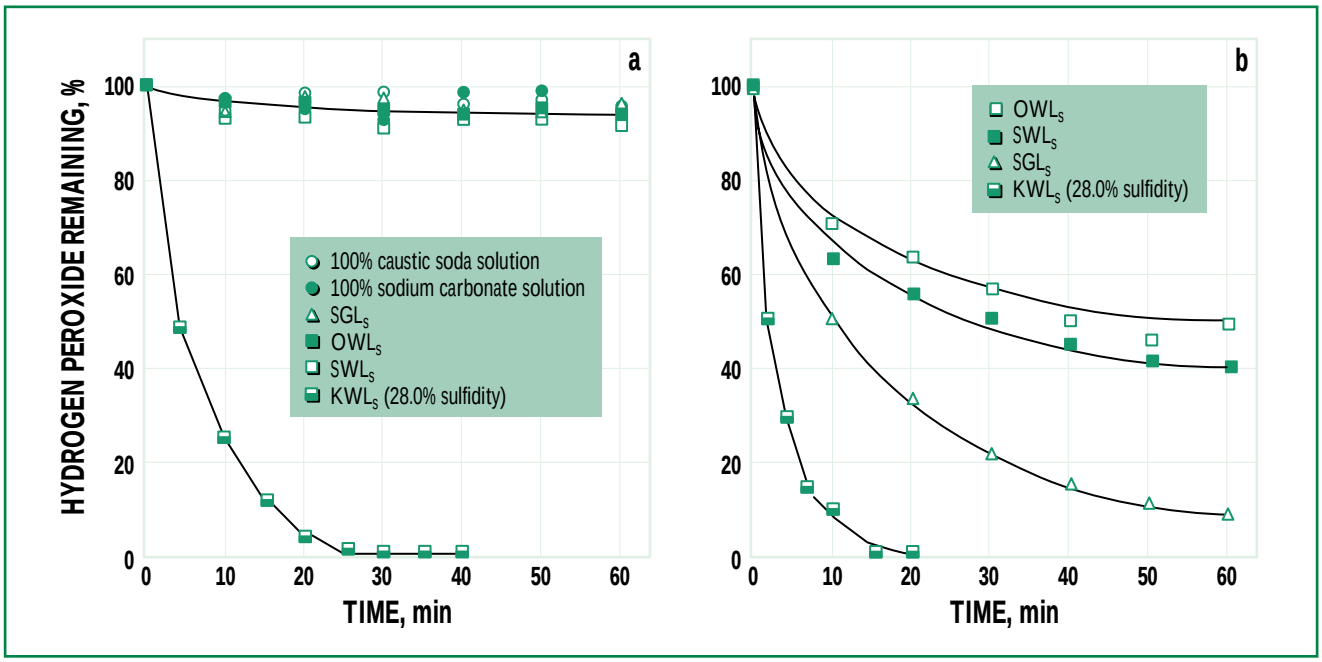
This work is an attempt to evaluate suitable alkalis to replace sodium hydroxide in EO, EP, and EOP extraction of pulps. Such alternatives will be critical to keep bleaching costs from escalating if the cost of sodium hydroxide increases as chlorine is eliminated as a pulp bleaching agent.

RESULTS AND DISCUSSION

Kinetics of peroxide decomposition in alkaline solutions

The rate of decomposition of hydrogen peroxide in synthetic and commercial (mill) liquors is illustrated in **Fig. 1**. Decomposition in sodium hydroxide, sodium carbonate, OWL_S, SWL_S, and SGL_S was slow, less than 10% over a 60-min period. In contrast, H_2O_2 decomposition was significant in the mill liquors—OWL_C, SWL_C, KWL_C, SGL_C—and in the synthetic KWL_S. Decomposition was rapid, completed within 15 min, in both KWL_S and KWL_C.

The expeditious decomposition of hydrogen peroxide in white liquor is due to sodium sulfide. This inference is derived from two observations: First, H_2O_2 decomposition was slow in synthetic OWL_S containing little sodium sulfide; second, decomposition was rapid in mill OWL_C, which contained a substantial



1. Decomposition of hydrogen peroxide in process alkalis: (a) synthetic liquors and (b) commercial (mill) liquors (H_2O_2 = 0.04 g·mole/L; temperature = 80°C)

Bleaching stages

C	= chlorination stage
D	= chlorine dioxide stage
E	= alkaline extraction stage
O	= oxygen-delignification stage
EO	= oxidative extraction
EP	= alkaline extraction with peroxide
EOP	= oxidative extraction with oxygen and peroxide
OP	= hydrogen peroxide-reinforced oxygen

Alkaline process liquors

KWL_S	= synthetic kraft white liquor
KWL_C	= commercial (mill) kraft white liquor
SWL_S	= synthetic soda white liquor
SWL_C	= commercial (mill) soda white liquor
SGL_S	= synthetic soda green liquor
SGL_C	= commercial (mill) soda green liquor
OWL_S	= synthetic oxidized white liquor
OWL_C	= commercial (mill) oxidized white liquor

1. Abbreviations for bleaching stages and alkaline process liquors

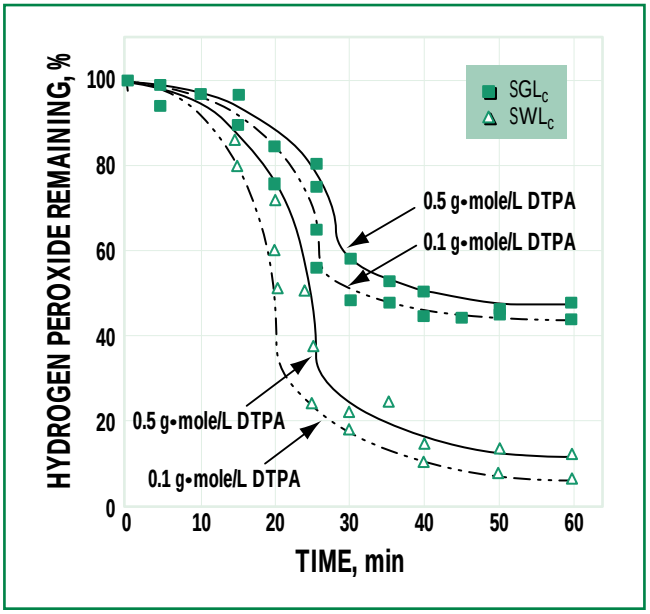
amount of sodium sulfide left from incomplete oxidation of KWL_C.

Decomposition of hydrogen peroxide in alkaline solutions containing only HO^- ions is first order in hydrogen peroxide and in nucleophile (OH^-) concentrations *(9)*. The order of the reaction becomes complex if more than one nucleophile takes part in the reaction. The decomposition of hydrogen peroxide in KWL is one such reaction (OH^-, HS^-, and S^{2-}). The reaction between hydrogen peroxide and a nucleophile occurs through an intermediate activated complex (Eq. 1). The rate of formation for the activated complex decides the extent of hydrogen peroxide decomposition *(10)*.

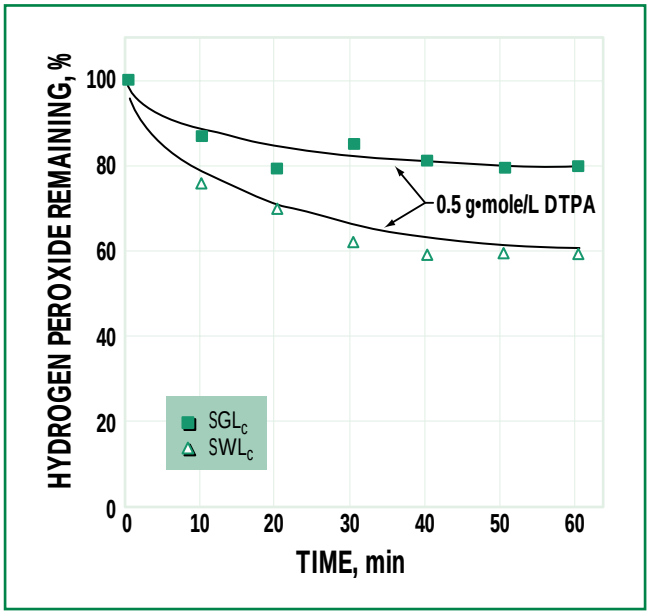
$$ROOH + N^- = [\text{activated complex}] = RO^- + HON \quad (1)$$

Evidently, the free energy of the nucleophile would decide the reactivity of the leaving group RO^- (in hydrogen peroxide, this would be HO^-) *(10)*. The dissociation products of alkaline sodium sulfide are hydrosulfide (HS^-) and sulfide (S^{2-}) ions. Both are strong nucleophiles. In the reaction between sodium sulfide and hydrogen peroxide, one of the nucleophiles, S^{2-} ion, has a large free energy. The leaving group HO^- ion has a high basicity. This is a combination that is bound to initiate strong decomposition of hydrogen peroxide and is probably the reason for its rapid decomposition in kraft white liquor.

The decomposition of hydrogen peroxide in nucleophiles of interest to this study is as follows: $S^{2-} > SO_3^{2-} > S_2O_3^{2-} > SO_4^{2-}$ *(11)*. SO_4^{2-} is the weakest nucleophile and would seldom initiate decomposition of hydrogen peroxide. The decomposition of hydrogen peroxide in S^{2-} has a second-order rate constant (k_2) of 1.5 L/mole·s that is 60 times higher than in $Na_2S_2O_3$ (k_2 = 2.5 x 10^{-2} L/mole·s) *(11)*. The rate constant in HO^- is 1 x 10^{-7} L/mole·s, indicating negligible decomposition in caustic solution. The decomposition of hydrogen peroxide in OWL should be negligible if all the Na_2S is converted to sodium sulfate (Na_2SO_4) (Fig. 1a). Even in OWL containing Na_2SO_4 and $Na_2S_2O_3$, the decomposi-



2. Effect of DTPA in stabilizing hydrogen peroxide in soda-mill white (SWL_C) and green (SGL_C) liquors (H_2O_2 = 0.04 g·mole/L; temperature = 80°C)



3. Effect of magnesium sulfate in stabilizing hydrogen peroxide in soda-mill white (SWL_C) and green (SGL_C) liquors (H_2O_2 = 0.04 g·mole/L; temperature = 80°C)

tion will be moderate, provided there is no sodium sulfide left unoxidized. The reason is the formation of the activated complex from the reaction between hydrogen peroxide and the nucleophile $S_2O_3^{2-}$. The formation may be slow, possessing less free energy to initiate and sustain the decomposition of hydrogen peroxide. The decomposition is more significant in OWL_C than in OWL_S because of residual sodium sulfide. When using OWL for EO, EP, or EOP extraction, it is important that all the sodium sulfide be converted to sodium sulfate and sodium thiosulfate. Thus KWL, synthetically prepared or otherwise, cannot be used in EO and EOP extraction of pulps.

Metal-ion-initiated decomposition of peroxide

Decomposition of hydrogen peroxide was negligible in synthetic SWL_S and SGL_S but significant in commercial SWL_C and SGL_C. The SWL_C and SGL_C are mixtures of sodium hydroxide and sodium carbonate, with a small amount of sodium sulfide. Therefore, the decomposition of hydrogen peroxide in these alkalis was unexpected. The decomposition may be the result of sources other than sodium sulfide, such as transition metals. Among the transition metals, manganese and iron are deleterious to hydrogen peroxide *(8)*. Analysis of SGL_C and SWL_C showed high concentration of manganese and iron, as seen in **Table II**. It was suspected that these materials came from the lime used in causticizing, and this was confirmed by testing reburned lime and makeup lime for manganese and iron. The analysis indicated that the iron concentration was 2000 mg/kg *(12)*. Poor purging of dregs, slaker rejects, and insufficient white-liquor clarification are all reasons for excessive amounts of transition metals in SGL_C and SWL_C.

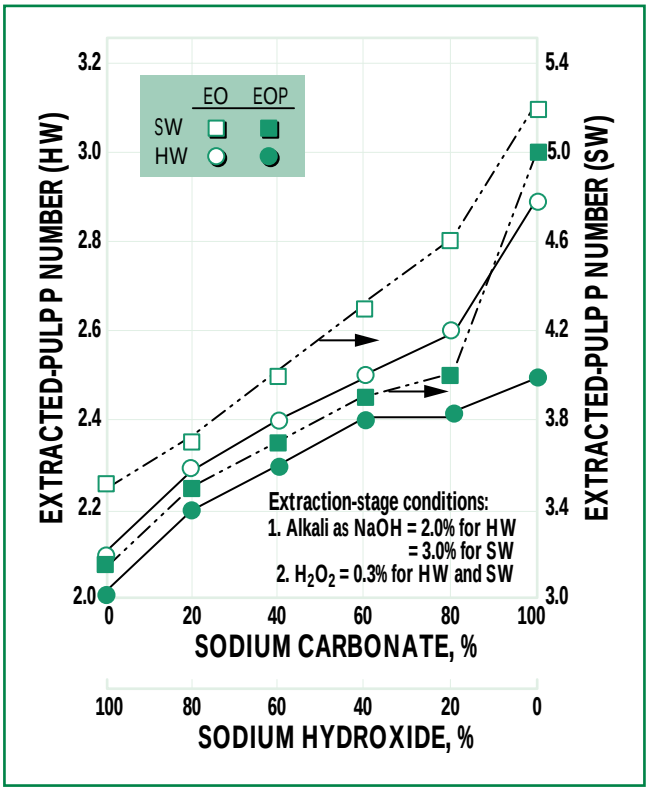
CONCENTRATION OF METALS ON ELEMENTAL BASIS, mg/kg

	Smelt	Green liquor from clarifier	Soda white liquor
Specific gravity	N.M.*	1.1	1.1
Iron	90.0	60.0	12.0
Manganese	90.0	80.0	28.0
Calcium	2000.0	55.0	<2.0
Magnesium	300.0	110.0	20.0

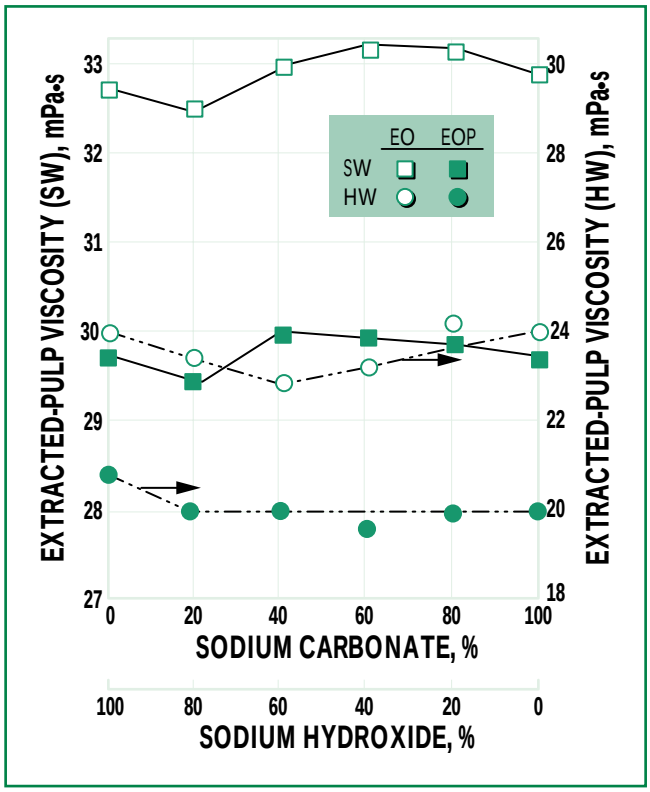
* Not measured

II. Concentration of transition metals in commercially obtained soda green liquor (SGL_C) and soda white liquors (SWL_C)

The mill SGL_C contained a substantial amount of manganese, as seen in Table II. Green-liquor clarification is of little help in removing manganese *(13)*. Pressure filtration is recommended to achieve manganese contents of less than 1 ppm in green liquor *(13)*. The slaking and the subsequent white-liquor clarification should help in its removal. However, the concentration of manganese is still high enough to initiate decomposition of hydrogen peroxide. This would render SWL_C and SGL_C less useful in EO and EOP extraction. Many kraft mills that use



4. Permanganate number of EO- and EOP-extracted hardwood and softwood kraft pulps after extraction using various ratios of sodium hydroxide and sodium carbonate as alkali



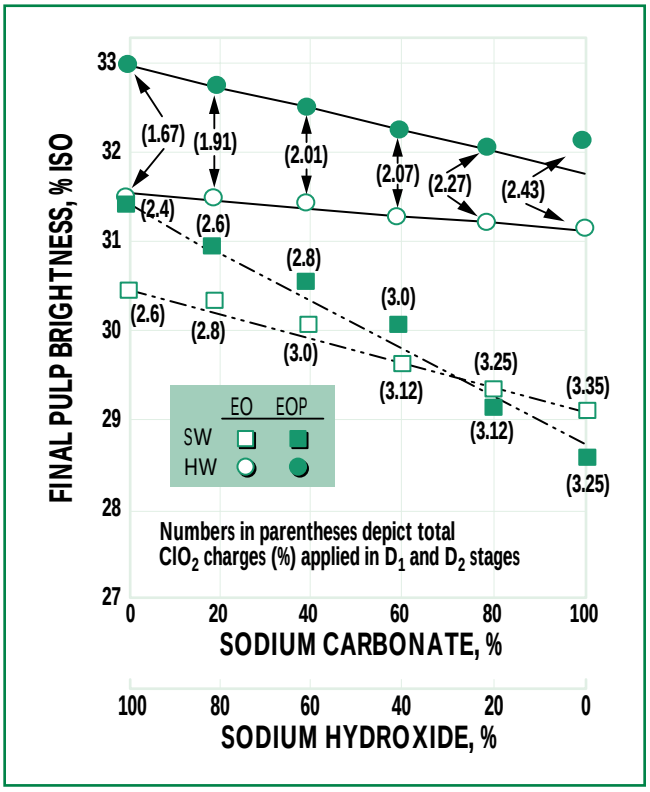
5. Viscosity of EO- and EOP-extracted hardwood and softwood kraft pulps after extraction using various ratios of sodium hydroxide and sodium carbonate as alkali (extraction-stage conditions as listed in Fig. 4)

OWL polish white liquor before oxidation. Pressure filtration of green liquor—combined with polishing of white liquor before oxidation—should lower the concentrations of transition metals in OWL_C *(13)*, making it useful for OP or EOP extraction of pulps.

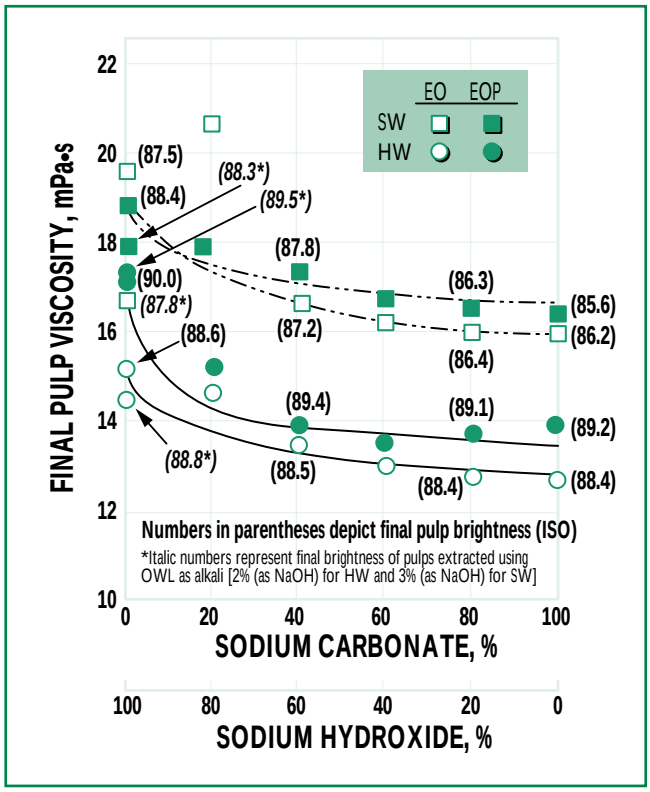
Mill OWL_C, SGL_C, or SWL_C containing normal amounts of transition metals can still be used in EO or EOP extraction by scavenging or masking the transition metals, thus slowing the decomposition of hydrogen peroxide. Allison *(14)* suggested the use of Na_5-DTPA (diethylenetriamine pentaacetic acid) because of its efficiency, particularly in scavenging iron and manganese.

The stability of hydrogen peroxide in SGL_C and SWL_C with added DTPA and $MgSO_4$ is depicted in **Figs. 2 and 3**, respectively. Magnesium salts provided better stabilization of hydrogen peroxide in alkaline solutions than DTPA. For example, in SGL_C containing Mg^{2+}, less than 40% of the hydrogen peroxide was decomposed compared with 90% when using DTPA. The decomposition was even less in SWL_C, probably because of the lower concentration of transition metals. Increasing DTPA application to 0.5 g·mole/L did not help in suppressing the rate of decomposition of hydrogen peroxide (Fig. 2).

Chelants are superior complexing agents and should have provided better protection for hydrogen peroxide than the magnesium salt. The opposite was observed in this study. The anomaly can be explained by the formation of Lewis bases. Under alkaline pH conditions, amine-based chelants form weak-base organic ligands (Lewis bases) with transition metals *(16)*. To prevent transition-metal-ion-initiated decomposition of hydrogen peroxide, the chelant should form strong ligands with these metals. For that, a high concentration of free metal ions is necessary *(15)*. Burton and Campbell *(16)* observed a strong decrease in concentration of free metal ions in alkaline solutions. They attributed this to poor dissociation of metal hydroxides into free metal and hydroxyl ions. It has been observed that in alkaline solutions, DTPA could efficiently chelate copper but not manganese or iron *(17)*. Therefore, by using DTPA, a substantial amount of iron and manganese may be left unchelated to react with and decompose hydrogen peroxide *(18)*. However, this does not explain the efficiency of Mg^{2+} salt over DTPA in slowing the decomposition of hydrogen peroxide. The initiation of metal hydroxo or oxo bridge by Mg^{2+}salt *(18)* is speculated to be the reason for its efficiency over DTPA in preventing transition-metal-initiated decomposition of hydrogen peroxide.



6. Final brightness and associated ClO_2 charges for EO- and EOP-extracted hardwood and softwood kraft pulps after extraction using various ratios of sodium hydroxide and sodium carbonate as alkali (first-extraction-stage conditions as listed in Fig. 4; additional extraction between D_1 and D_2 stages with 0.5% NaOH for 25 min at 70°C)



7. Final viscosity and brightness of EO- and EOP-extracted hardwood and softwood kraft pulps after extraction using various ratios of sodium hydroxide and sodium carbonate as alkali (extraction-stage conditions as listed in Fig. 4)

Alkaline extraction and multistage bleaching of pulps

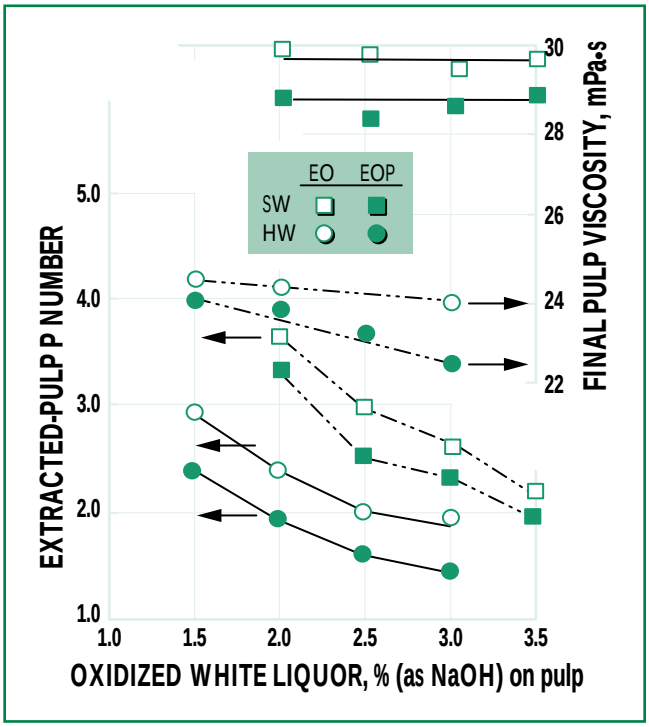
The low rate of hydrogen peroxide decomposition in OWL, SWL, and SGL shows that these alkalis can be substituted for sodium hydroxide in EO and EOP extraction of pulp. Neither synthetic nor mill KWL can be used in the oxidative extraction of pulp. Many mills polish their white liquor, using oxygen for oxidation of the white liquor. Therefore, it is fair to assume that the OWL_C will have little transition metal ions and residual sodium sulfide. The SWL and SGL liquors—available from soda or soda–AQ mills—are mainly mixtures of sodium hydroxide and sodium carbonate.

The efficacy of sodium carbonate and sodium hydroxide mixtures in the alkaline extraction and bleaching of hardwood (HW) and softwood (SW) pulps is depicted in **Figs. 4–7**.

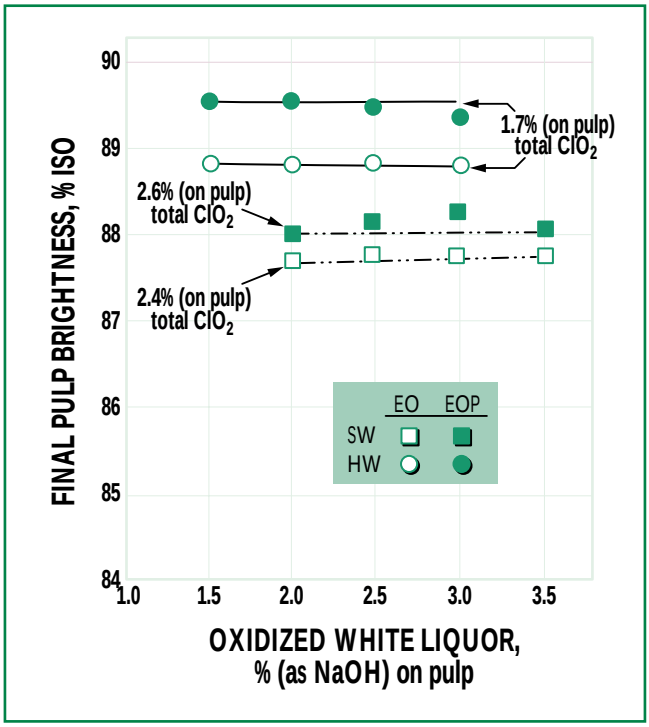
Clearly, sodium carbonate alone cannot be used for the extraction of pulps and must be augmented with sodium hydroxide. The permanganate number of sodium carbonate-extracted pulps (CE P number) was 30–60% higher than sodium hydroxide-extracted pulp, as seen in Fig. 4. Hydrogen peroxide reinforcement of the EO stage (i.e., EOP extraction) helped in decreasing the CE P number by about 10%. Until up to 80% sodium carbonate substitution, the increase in CE P number for the EO- and EOP-extracted pulps was gradual, but CE P number increased sharply when substitution exceeded 80%. The difference in extracted pulp viscosity from 100% sodium hydroxide to 100% sodium carbonate extraction was insignificant, as seen in Fig. 5. However, reinforcement of the EO stage with hydrogen peroxide profoundly influenced the viscosity. The EOP-extracted pulps had 15% lower viscosity, irrespective of the alkali used. The results for CE P number and viscosity indicate that extraction with 50:50 or 60:40 sodium hydroxide and sodium carbonate offered better selectivity[1] than either 100% sodium carbonate or 100% sodium hydroxide extraction of pulps.

Extracted-pulp brightness followed a similar trend as CE P number, decreasing progressively as the alkali changed from 100% sodium hydroxide to 100% sodium carbonate. It seems obvious that to reach a given final pulp brightness, the demand for chlorine dioxide at the final D stage(s) would be higher for pulps extracted with 100% sodium

[1]Selectivity is defined as the ratio of pulp viscosity (representing carbohydrate degradation) to kappa or permanganate number (representing the extent of lignin removal) for a particular pulping or bleaching process *(19)*.



8. Permanganate number and final viscosity of EO- and EOP-extracted hardwood and softwood kraft pulps after extraction using oxidized white liquor as alkali (H_2O_2 charge in EOP = 0.3% for HW and SW)



9. Final pulp brightness of EO- and EOP-extracted hardwood and softwood kraft pulps after extraction using oxidized white liquor as alkali (H_2O_2 charge in EOP = 0.3% for HW and SW; additional extraction between D_1 and D_2 stages with 0.5% NaOH for 25 min at 70°C)

carbonate because of the higher CE P number and lower brightness. This was confirmed by the lower final brightness for 100% sodium carbonate-extracted pulps, as seen in Fig. 6. Also, EO-extracted pulps suffered a profound decrease in final brightness compared with EOP-extracted pulps, as seen in Fig. 6. For the EOP-extracted hardwood pulps, 100% NaOH treatment provided the highest brightness at the lowest chlorine dioxide discharge (90% ISO brightness at 1.67% ClO_2). In contrast, the pulp treated with 100% sodium carbonate required 50% more chlorine dioxide to acheive a lower brightness (89.2% ISO at 2.43% ClO_2). Hardwood pulps experienced higher brightness gain than softwood pulps from the hydrogen peroxide reinforcement.

There is a sharp drop in the final viscosity of pulp when the alkali mix was changed from 100:0 to 80:20 sodium hydroxide and sodium carbonate, as seen in Fig. 7. Beyond this ratio, the change in viscosity was small and insignificant. Again, EOP-extracted pulps had higher brightness and viscosity than EO-extracted pulps. The hardwood pulps were bleached to higher brightness (Fig. 6) but lower viscosity (Fig. 7) than softwood pulps.

Peroxide-reinforced oxidative extraction using OWL as alkali during multistage bleaching

It has been reported that many mills use pressure filtration to remove metal ions and to polish green liquor before the causticizing reaction *(20)*. Mills are also filtering their white liquor to avoid introducing metal ions to the pulp through the cooking liquor. This is crucial to elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching of pulps *(13, 20)*. The synthetic oxidized white liquor (OWL_s) fulfills two objectives. One, it simulates the oxidized-white-liquor preparation from filtered and polished white liquor containing few metal ions, and two, it is a fully oxidized white liquor containing very little sodium thiosulfate. The results of using oxidized white liquor as an alternative alkali to sodium hydroxide is depicted in **Figs. 8 and 9**.

OWL is as good as 100% sodium hydroxide in providing low CE P numbers, as seen by comparing the results in Fig. 4 with those in Fig. 8. A CE P number as low as 2.0 is possible from EOP extraction of softwood pulps by using 3.5% OWL (NaOH equivalent). At any given OWL

KEYWORDS
Alkali extraction, alkaline pulps, alkalis, bibliographies, carbonates, chemical degradation, chemical pulps, chemical reactions, cooking liquors, degradation, evaluation, extraction, hydrogen peroxide, hydroxides, kraft liquors, kraft pulps, peroxides, separation, soda liquors, sodium carbonate, sodium compounds, sodium hydroxide, substitutes, white liquors.

	KWL_S	OWL_S	KWL_C	OWL_C	SWL_S	SWL_C	SGL_S	SGL_C[a]
Sodium hydroxide	65.0	82.5	71.7	79.0	100.0	98.7	20.0	21.4
Sodium sulfide	35.0	0.0	26.8	3.5	…	0.3	…	0.6
Sodium carbonate	25.0	25.0	21.3	24.3	25.0	22.5	98.0	96.8
Sodium thiosulfate	3.0	20.5	4.0	20.5	0.0	N.D.[b]	…	N.D.[b]
Sodium sulfate	9.0	36.0	9.1	32.4	0.0	N.D.[b]	0.0	N.D.[b]
Sodium sulfite	4.5	0.0	2.5	N.D.[b]	0.0	N.D.[b]	0.0	N.D.[b]
Active alkali [c]	100.0	82.5	98.5	79.0	100.0	99.0	15.0	22.0
Effective alkali [d]	82.5	82.5	85.1	80.2	…	98.9	…	21.7
Total titratable alkali [e]	125.0	107.5	119.8	106.8	125.0	121.5	118.0	118.8

[a] The commercial soda green liquor (SGL_C) is collected from the outlet of the green-liquor clarifier before the slaker.
[b] Not determined
[c] Active alkali (for KWL_S, OWL_S, KWL_C, and OWL_C) = NaOH + Na_2S [all expressed in units of g/L (as Na_2O)]
[d] Effective alkali (for KWL_S, OWL_S, KWL_C, and OWL_C) = NaOH + 0.5 Na_2S [all expressed in units of g/L (as Na_2O)]
[e] Total titratable alkali (for KWL_S, OWL_S, KWL_C, and OWL_C) = NaOH + Na_2S + Na_2CO_3 [all expressed in units of g/L (as Na_2O)]

III. Composition of alkaline liquors, g/L (as Na_2O)

charge, the CE P number was lower for EOP-extracted than for EO-extracted pulps. However, the EO-extracted hardwoods had a lower CE P number than the EOP-extracted softwoods. The hardwood pulp can be EOP-extracted to less than 1.5 CE P number by using 2.5% OWL (NaOH basis).

The EOP-extracted pulps had lower viscosity than EO-extracted pulps, as seen in Fig. 8. Increasing OWL charge did not change the viscosity of EO- or EOP-extracted softwood pulps. In contrast, the viscosity of extracted hardwood pulps decreased with increasing OWL charge, although the decrease was small and insignificant.

Reinforcement of the extraction stage with hydrogen peroxide had a strong influence on the extracted-pulp brightness of hardwood pulps but little effect on softwood pulps, as seen in Fig. 9. The final pulp brightness of EO- and EOP-extracted hardwood and softwood pulps using OWL as alkali was comparable with the brightness obtained for pulps extracted with mixtures of sodium hydroxide and sodium carbonate. The final brightness of softwood pulp was lower than hardwood pulps. At equivalent NaOH charge for the EO and EOP stages (2% for HW and 3% for SW), the final brightness of OWL-treated hardwood and softwood pulps was comparable with the NaOH-treated pulps. The final viscosity from OWL-extracted and bleached hardwood and softwood pulps was higher than the bleached pulps from 100% sodium hydroxide and 100% sodium carbonate extraction.

CONCLUSIONS

Neither synthetic nor commercial kraft white liquors are suitable for use in oxidative extraction (EO or EOP) of pulps. Both liquors show strong sodium sulfide-initiated decomposition of hydrogen peroxide. In sodium sulfide-free alkalis, it is important to scavenge transition metals to minimize the decomposition of hydrogen peroxide. Magnesium salts are better than DTPA in scavenging the metals in soda-mill white and green liquors.

Extraction of pulps using synthetically prepared oxidized white liquor (simulating the oxidized kraft liquor prepared from filtered white liquor and oxidized to complete conversion of sodium sulfide) provided results equivalent to 100% sodium hydroxide. Oxidative extraction of hardwood and softwood kraft pulps with mixtures of sodium hydroxide and sodium carbonate (simulating soda white liquor and soda green liquor) showed that sodium carbonate alone cannot be used as an alkali and must be extended with sodium hydroxide. Sodium hydroxide and sodium carbonate mixtures (50/50 or 60/40) can replace 100% sodium hydroxide as alkali in the EO and EOP extraction of pulps.

The maximum pulp brightness obtained from bleaching 100% sodium carbonate-extracted pulp was 86–87% ISO, and this brightness was achieved at the cost of using 20–30% more chlorine dioxide in the final D stages. Sodium carbonate extraction and DED bleaching of hardwood and softwood pulp also produced a pulp with lower final viscosity than the sodium hydroxide-extracted pulps. When oxidized white liquor was used in EO and EOP extraction, the drop in the viscosity of final bleached pulps was small and insignificant.

EXPERIMENTAL

Preparation and characterization of alkaline liquors

ACS-grade ultrapure chemicals were used in the preparation of synthetic KWL_S, SWL_S, SGL_S, and OWL_S. The liquors were prepared to the concentrations suggested by Green *(21)*. The commercial mill liquors (SWL_C, SGL_C, KWL_C, and OWL_C) were obtained from a southern soda–AQ mill and a midwestern kraft mill. The liquors were analyzed by TAPPI Test Method T 624 cm-85. The OWL_C contained significant amounts of sodium sulfide. The compositions of the synthetic and commercial liquors are listed in **Table III.**

	HARDWOOD (kappa no. 20.4)			SOFTWOOD (kappa no. 31.2)	
Chlorination (C/D stage)					
Chlorine dioxide substitution in first stage, %	…	40.0		…	
Kappa factor	0.20	…		0.22	
Consistency, %	…	8.0		…	
Temperature, °C	…	55.0–57.0		…	
Reaction time, min	…	20		…	
Oxidative extraction (EO or EOP stage) [b]					
Oxygen, %	…	1.5		…	
Hydrogen peroxide, %	…	0–0.3		…	
	TYPE OF ALKALI				
	$NaOH/Na_2CO_3$ (0–100/100–0)	**OWL**		**$NaOH/Na_2CO_3$ (0–100/100–0)**	**OWL**
Alkali charge (as NaOH), %	2.0	1.5–3.0		3.0	2.0–3.5
Consistency, %	…	…	12.0	…	…
Temperature, °C	…	…	70.0	…	…
Reaction time, h	…	…	1.0	…	…
Extracted kappa number					
EO stage	2.1–4.8	2.1–3.0		3.7–5.2	2.3–3.8
EOP stage	2.0–4.0	1.6–2.5		3.2–5.0	2.1–3.3
Brightness, % ISO					
EO-extracted pulp	40.2–44.1	40.4–42.5		26.0–36.1	34.0–35.0
EOP-extracted pulp	44.1–47.0	45.1–46.3		31.0–38.1	35.5–37.0
CED viscosity, mPa·s					
EO-extracted pulp	22.8–24.1	24.0–24.2		32.8–32.9	29.5–30.0
EOP-extracted pulp	20.0–21.0	22.3–24.0		29.8–29.9	28.4–29.0
First chlorine dioxide (D1 stage)					
Chlorine dioxide charge as (ClO_2), %					
EO-extracted pulp	1.0–1.43	1.0		1.6–2.35	1.6
EOP-extracted pulp	1.0–1.43	1.0		1.4–2.25	1.4
Consistency, %	…	…	12.0	…	…
Temperature, °C	…	…	85.0	…	…
Reaction time, h	…	…	4.0	…	…
Residual ClO_2, ppm	20–140	Trace		N.M.[c]	30–180
Brightness, % ISO	72.6–81.0	76.2–80.6		66.8–80.7	75.3–80.1
CED viscosity, mPa·s	16.7–21.0	20.0–22.3		22.8–25.6	23.0–26.8
Second alkaline extraction (E2 stage)					
Alkali charge (as NaOH), %	…	…	0.5	…	…
Consistency, %	…	…	12.0	…	…
Temperature, °C	…	…	70.0	…	…
Reaction time, min	…	…	25	…	…
pH (out)	10.2–10.5	N.M.[c]		9.8–10.8	10.5–10.9
Second chlorine dioxide (D2 stage)					
Chlorine dioxide charge as (ClO_2), %					
EO-extracted pulp	0.67–1.0	0.7		…	1.0 …
EOP-extracted pulp	0.67–1.0	0.7		…	1.0 …
Consistency, %	…	…	12.0	…	…
Temperature, °C	…	…	85.0	…	…
Reaction time, h	…	…	2.0	…	…
Residual ClO_2, ppm	41–152	N.M.[c]		21–88	N.M.[c]
Brightness, % ISO	88.4–90.0	88.8–89.5		85.6–88.4	87.8–88.3
CED viscosity, mPa·s	13.0–17.3	14.7–17.6		16.6–19.8	16.5–18.0

[a] Data columns that are centered between blank lines apply to all of the blank spaces. All chemical charges are on oven-dry pulp basis.
[b] 0.5% $MgSO_4$ charge to EO and E(OP) extraction
[c] Not measured

IV. Bleaching conditions and pulp properties[a]

Decomposition of hydrogen peroxide

Decomposition of hydrogen peroxide was carried out in a modified Parr reactor *(22)* using the oxygen supply port for the withdrawal of samples for analysis. The acidic titanium sulfate (titanium oxysulfate–monosulfuric acid octahydrate complex) titration *(23, 24)* used for the measurement of residual peroxide was simpler than the iodide–thiosulfate method *(25)*.

Extraction and bleaching of HW and SW pulps

The bleaching conditions and the pulp properties are detailed in **Table IV**. Chlorine dioxide substitution at the first stage was 40%, and kappa factor application was 0.20 and 0.22, respectively, for hardwood and softwood pulps. Alkali application for extraction of pulps was on NaOH basis. **TJ**

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