The use of oxidized white liquor as a caustic replacement in O, E_O, E_{OP}, and E_2 bleaching stages of kraft hardwood and softwood pulp

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ABSTRACT

The use of oxidized white liquor as an alkali source in bleaching sequences can serve to maintain a kraft mill's chemical balance. If the oxidized white liquor is of sufficiently high quality (i.e., no sodium sulfide and limited thiosulfate present), it can be used as an alkali source in any bleaching stage that would normally require sodium hydroxide.

The oxidized white liquor used in this study (Q-OWL™) was prepared at a pilot plant located at a kraft mill using a stream of the mill's white liquor. Analysis of this oxidized white liquor gave results indicating no sodium sulfide present and greater than 90% conversion to sodium sulfate. The Q-OWL was compared to both NaOH and unoxidized white liquor as a caustic source in O, E_O, E_{OP}, and E_2 stages of kraft hardwood and softwood bleaching sequences. In all cases, the Q-OWL resulted in equivalent or higher brightness and viscosity values than those obtained using caustic, and both Q-OWL and NaOH gave better results than those obtained using white liquor. Results are also presented from a 50-gal/min plant trial unit, where the OWL produced was used in the kraft mill's E_2 stage.

Application:

Oxidized white liquor can provide economic and environmental advantages when used to replace caustic in delignification and bleaching stages.

THE ENVIRONMENTAL CONSTRAINTS placed on today's kraft mills have led to the implementation, at many mills, of 100% chlorine dioxide substitution and oxygen delignification stages. Both of these additions have had an impact on chemical balances in the mill. The increased chemical from ClO_2 generator by-products may result in a surplus of white liquor. Many mills currently sewer this excess by-product saltcake. The use of white liquor as an alkaline source in oxygen delignification and extraction stages is a means to reduce direct caustic purchase as well as provide a sulfur and trace metal purge via the bleach plant effluent after further use rather than directly from the chlorine dioxide generator.

The literature is not in agreement as to the effects of using white liquor (WL) as the source of caustic in an oxygen delignification stage. Some studies *(1, 2)* have indicated that WL can be used interchangeably with NaOH in medium-consistency oxygen delignification (MCOD) stages with no effect on the resulting delignification rates or pulp properties. However, others *(3–5)* claim that the Na_2S present in the white liquor degrades the pulp carbohydrates. Another potentially major problem with the use of white liquor is the formation of hydrogen sulfide when the liquor pH drops below 10.

The problems encountered with pulp degradation and hydrogen sulfide formation can be eliminated by converting the sodium sulfide to either sodium thiosulfate or sodium sulfate through oxidation to produce oxidized white liquor (OWL). OWL has been used successfully in the oxygen delignification stage. A study performed by Ayala *et al. (6)* compared OWL to both WL and NaOH in an MCOD. Their findings indicated that OWL resulted in a higher total pulp yield at a given final kappa number compared to NaOH or WL. Fully oxidized white liquor (i.e., sulfide converted to sulfate) gave a pulp of equivalent brightness to that obtained with NaOH.

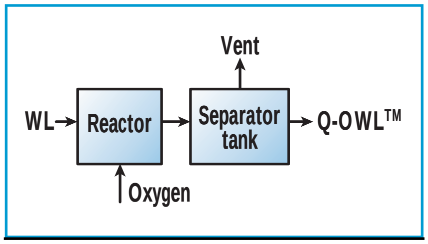
The use of OWL in extraction or peroxide bleaching stages has been debated. This is primarily due to concern regarding the effect of sulfur compounds and any transition metals that may be present on the decomposition of peroxide. Parthasarathy *(7)* reported that the decomposition of peroxide in OWL containing both thiosulfate and sulfate is moderate. His study indicated that the OWL could be used in E_O and E_{OP} stages.

The polarized points of view in the literature regarding the suitability of OWL in delignification, and particularly peroxide-containing bleaching stages, served as motivation for this study. Quantum Technologies had developed a system for oxidizing white liquor that consisted of a very efficient reactor. This reactor produced a white liquor that contained no sodium sulfide and more than 90% conversion to sulfate. This oxidized white liquor (Q-OWL™) was used as an alkali source for oxygen delignification, extraction, and peroxide bleaching stages. The results were compared to those obtained using either NaOH or WL.

EXPERIMENTAL

Q-OWL generation

White liquor and Q-OWL samples



1. Schematic of Q-OWL pilot-plant system

Pulp	Brightness, % GE	Viscosity, cp	Kappa no.
Hardwood 1	29.8	26.7	13.0
Hardwood 2	27.4	27.5	14.5
Softwood	23.6	26.8	25.9

I. Starting pulp characteristics

were obtained from Quantum's pilot-plant facility. This facility operated on a slipstream of white liquor from a kraft pulp mill. The white liquor stream entered a very efficient gas/liquor reactor, where it was mixed with oxygen. The OWL then exited the reactor and went into a separator tank. In the pilot-plant system used for these experiments, the gases from the separator tank were vented to the atmosphere. Under normal operation, the gases would be recirculated to the reactor. The oxidation reaction is highly exothermic, and the reaction time is very short. The exothermic heat of reaction is recoverable either by use of the hot oxidized white liquor or via the optional heat exchanger. A diagram of the pilot-plant facility is shown in **Fig. 1.**

Both the incoming white liquor (WL) and exiting Q-OWL were analyzed for NaOH content and sulfur-containing species composition by TAPPI Test Method T 624 cm-85.

Bleaching procedures

The pulp used for this study consisted of both hardwood and softwood brownstock obtained from a kraft mill. Three different brownstock samples were used. The characteristics of these starting pulps are given in **Table I.**

The pulp samples were well washed and then used without further treatment. Bleaching studies were performed using a Quantum Mark V High Intensity Mixer/Reactor equipped with either a hastelloy or Teflon-coated stainless steel mixing bowl and rotor.

Several different types of bleaching sequences wee studied. Hardwood sequences investigated were $DE_{OP}D$, $ODE_{O}D$, $ODE_{OP}D$, $ODE_{O}P$, and $ODE_{OP}P$. The softwood sequences were $ODE_{O}DED$ and $ODE_{OP}DED$. When WL or Q-OWL was used as an alkali source, it was used in all stages in the sequence that required caustic. The alkali application for the WL and Q-OWL was on an NaOH basis. In all cases, filtrate carryover was used to simulate mill washing conditions and to evaluate the effect that any carryover would have on subsequent bleaching stages. This was done by saving filtrate from a given bleaching stage, washing the pulp thoroughly, and then adding a sufficient quantity of filtrate back to the pulp in the next stage to simulate a 10% filtrate carryover. The bleaching conditions used for these experiments are given in **Table II.**

Pulp viscosities were determined by TAPPI Test Method T 230 om-94, kappa numbers by T 236 cm-85, and brightness measurements by T 452 om-92.

RESULTS AND DISCUSSION

Composition of WL and Q-OWL

The results of the analysis of a typical sample of both the starting white liquor and the Q-OWL are shown in **Table III.** These data indicate that all of the sodium sulfide present in the white liquor was oxidized. Greater than 90% of the original sodium sulfide present was oxidized to sulfate.

Hardwood $DE_{OP}D$ sequence

The first set of experiments conducted using the Q-OWL investigated its use in a peroxide-reinforced oxidative extraction stage. These experiments were conducted to determine if the small amounts of sodium thiosulfate and sodium sulfite present in the Q-OWL had a deleterious effect on the peroxide performance.

The sample denoted Hardwood 1 was used for these experiments. The bleaching results are presented in **Table IV.** Graphs depicting the brightness and viscosity of the bleached pulp samples appear in **Figs. 2 and 3,** respectively.

As can be seen from both the data and the graphs, the Q-OWL gave slightly higher final brightness values and about a 2-point-higher viscosity than the samples that used NaOH as the alkali source. A trace quantity of peroxide was present in the filtrate of the E_{OP} stage of both the NaOH and Q-OWL samples. This demonstrates that any residual thiosulfate and sulfite present in the Q-OWL did not cause decomposition of the peroxide. By contrast, the WL showed a zero peroxide residual.

The brightness and viscosity of the WL sample was considerably lower than those obtained with either the NaOH or the Q-OWL.

Softwood $ODE_{O}DED$ and $DE_{OP}DED$ sequences

To further investigate the effect of using Q-OWL in other types of bleaching stages, a series of experiments were performed on a softwood brownstock. This pulp was subjected to a full bleaching sequence, where the alkali source was used in all bleaching stages that required it (i.e., O, E_O, E_{OP}, E_2) and as a caustic buffer if needed in the D stages. **Tables V–VIII** are a summary of the bleaching results for these sequences. As indicated by these results, the Q-OWL performed at least as well as the NaOH in all cases of brightness development and final pulp viscosity. As was the case in the previous hardwood samples, the WL gave inferior results to either the NaOH or Q-OWL. The brightness and viscosity results for the $ODE_{OP}DED$ sequence are depicted in **Figs. 4 and 5.** Similar results were obtained for the ODE$_O$DED sequence.

Hardwood ODE$_O$D, ODE$_O$P, ODE$_{OP}$D, and ODE$_{EO}$P sequence

An additional set of experiments was conducted on a new hardwood brownstock sample, Hardwood 2. An oxygen delignification stage was run on this brownstock under more severe conditions than those used for the softwood sample. The applied caustic level, the reaction time, and the temperature were all increased as means to achieve a higher degree of delignification. The kappa number was reduced by more than 40% under these conditions. The oxygen-delignified pulp was then subjected to a 100% D stage and followed by either E$_O$D, E$_O$P, E$_{OP}$D, or E$_{OP}$P. By using these sequences, it was possible to determine the effect of the alkali source on peroxide delignification and bleaching capabilities. As in the previous experiments, either NaOH, Q-OWL, or WL were used in all stages requiring alkali. The bleaching results appear in **Tables IX–XI.** Examples of typical results obtained are shown in **Figs. 6–9,** which give the brightness and viscosity of ODE$_{OP}$D and ODE$_{OP}$P sequences.

Once again, the results indicate that the oxidized white liquor produced both brightness and viscosity results similar to those obtained using the caustic. For the ODE$_O$D and ODE$_{OP}$D sequences, the WL gave a pulp with slightly lower brightness and about a 2-point-lower viscosity than that obtained with either the NaOH or Q-OWL. A more dramatic difference was noted on the two sequences containing a P stage. Here, the WL sample yielded a pulp with 1–2 points lower brightness than that obtained with the other alkali sources. The Q-OWL pulp had a higher viscosity than either NaOH or WL. The data support the position that white liquor is not suitable as a caustic replacement because it degrades the carbohydrate, as evidenced by the lower pulp viscosity. Also, the sodium sulfide present in the white liquor reacts with peroxide and results in a lower-brightness pulp. Conversely, the oxidized white liquor used for these experiments showed evidence of protecting the carbohydrates. The samples that used Q-OWL demonstrated a higher viscosity than that obtained with NaOH while maintaining at least equivalent brightness.

Sequence: DE$_{OP}$D
Starting pulp: Hardwood brownstock 1

Parameter	STAGE D	STAGE E$_{OP}$	STAGE D
Chemical	1.37% ClO_2	1.55% NaOH 0.5% H_2O_2 20 psig O_2	0.8, 1.0, 1.2% ClO_2
Time, min	30	40	180
Temperature, °C	50	75	75
Consistency, %	10	10	10

Sequence: ODE$_O$DED and ODE$_{OP}$DED
Starting pulp: Softwood brownstock

Parameter	O	D	E$_O$ or E$_{OP}$	D	E$_2$	D
Chemical	2.0% NaOH; 100 psig O_2	1.8% D	1.9% NaOH; 0.8% H_2O_2 (E$_{OP}$)	0.8, 1.0, 1.2, 1.4% ClO_2	0.5% NaOH	0.5% ClO_2
Time, min	15	30	40	180	60	180
Temperature, °C	90	50	75	75	70	75
Consistency, %	10	10	10	10	10	10

Sequence: ODE$_O$D, ODE$_O$P, ODE$_{OP}$D, and ODE$_{OP}$P
Starting pulp: Hardwood brownstock 2

Parameter	O	D	E$_O$ or E$_{OP}$	D or P
Chemical	2.5% NaOH; 100 psig O_2	0.64% D	0.8% NaOH; 0.5% H_2O_2 (E$_{OP}$) O_2 = 20 psig	0.6, 0.8, 1.% ClO_2 0.8, 1.0, 1.2% H_2O_2
Time, min	45	30	30	90
Temperature, °C	110	50	80	80
Consistency, %	12	12	12	12

II. Bleaching conditions

Type	NaOH	Na_2S	$Na_2S_2O_3$	Na_2SO_3	Na_2SO_4
	CONCENTRATION, g/L as Na_2O				
WL	58.9	30.8	1.61	1.50	3.54
Q-OWL	62.0	0	2.81	1.70	30.50

III. Typical analysis of white liquor and Q-OWL

Plant bleaching results

Laboratory bleaching results can be a good indication of

D_0 stage

Parameter	Result
Brightness, %GE	56.7
Viscosity, cp	27.1

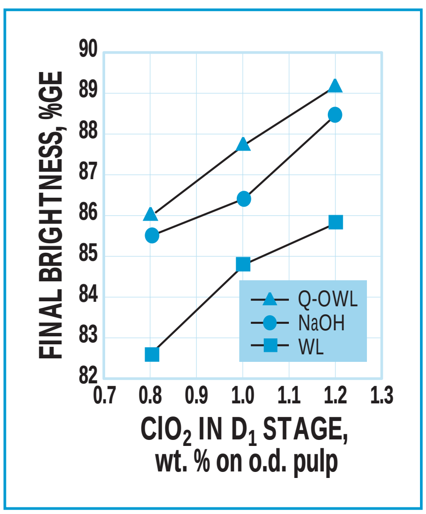
E_{OP} stage

	SAMPLE		
Parameter	NaOH	WL	OWL
Final pH	11.8	11.5	11.5
Residual H_2O_2	Trace	0	Trace
Brightness, %GE	71.9	66.1	71.9
Viscosity, cp	22.8	34.0	20.8
Kappa no.	2.9	3.4	2.9

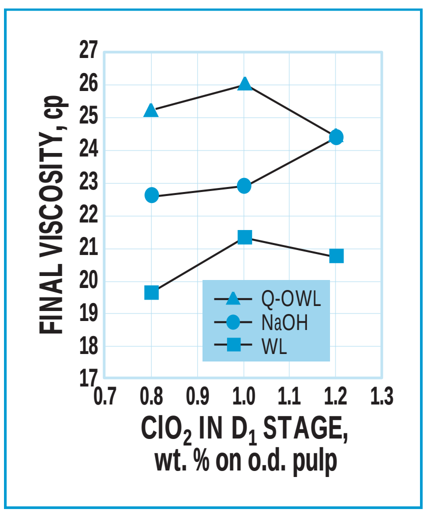
D_1 stage

					D, %				
Parameter	0.8	1.0	1.2	0.8	1.0	1.2	0.8	1.0	1.2
Viscosity, cp	19.6	21.3	20.7	22.6	22.9	24.4	25.2	26.0	24.4
Brightness, %GE	85.5	86.4	88.4	82.6	84.8	85.8	86.0	87.7	89.1
Rev. brightness, %GE	82.7	82.9	85.4	79.7	81.5	82.4	83.9	85.2	86.4

IV. Hardwood $DE_{OP}D$ bleaching results. Starting pulp: hardwood brownstock 1.



2. $DE_{OP}D$ sequence brightness vs. D_1 charge, hardwood sample 1



3. $DE_{OP}D$ sequence viscosity vs. D_1 charge, hardwood sample 1

what to expect from a particular bleaching sequence. However, what ultimately matters are the results obtained in a bleach plant. A 50-gal/min plant-trial Q-OWL unit was positioned at a kraft mill, where it operated for a total of about 6 days. During this time, the OWL produced was used in the bleach plant's E_2 extraction stage on both hardwood and softwood pulps. The results obtained using the OWL were compared to those obtained using both NaOH and WL. The brightness results, the D_2 application rates, and D_2 viscosity values appear in **Table XII.**

The D_2 application rate, the brightness, and the viscosity all indicate that the Q-OWL performed satisfactorily in the mill's extraction stage. In addition, the mill's operators noted no difference in performance of the bleaching sequence when the OWL was used. They could not tell when it entered the mill. In all respects, it functioned identically to NaOH.

CONCLUSIONS

The following conclusions were made based on the experiments discussed:

- The use of oxidized white liquor as an alkali source for oxygen delignification, extraction, and peroxide bleaching stages can reduce caustic purchase while providing a convenient purge of sulfur and trace metals. The white liquor thus helps preserve a mill's sodium/sulfur balance.
- The Quantum Q-OWL process

Parameter	CAUSTIC SOURCE NaOH	WL	Q-OWL
Brightness, %GE	24.7	25.0	25.2
Viscosity, cp	22.2	21.0	22.0
Kappa no.	21.0	21.6	20.2

V. Softwood bleaching results after oxygen delignification stage

	E_O			E_{OP}		
	CAUSTIC SOURCE					
Parameter	**NaOH**	**WL**	**Q-OWL**	**NaOH**	**WL**	**Q-OWL**
Brightness, % GE	51.3	50.3	53.2	61.3	57.7	62.1
Viscosity, cp	19.6	16.7	16.8	18.3	17.1	18.0
Kappa no.	4.4	4.5	4.2	3.6	4.0	3.7

VI. Softwood bleaching results after ODE$_O$ and ODE$_{OP}$ stages

	CAUSTIC SOURCE											
	NaOH				WL				Q-OWL			
	D, %											
Parameter	**0.8**	**1.0**	**1.2**	**1.4**	**0.8**	**1.0**	**1.2**	**1.4**	**0.8**	**1.0**	**1.2**	**1.4**
D$_1$ stage												
Brightness, %GE	78.2	79.6	81.3	81.4	75.5	78.0	80.4	81.1	80.0	79.3	81.5	83.3
Viscosity, cp	19.1	19.2	18.3	17.0	18.0	17.5	17.9	17.0	19.5	19.8	19.9	20.4
E$_2$ stage												
Brightness, %GE	75.4	77.0	78.2	79.0	72.3	73.2	76.3	77.2	78.3	-	79.3	80.7
Viscosity, cp	18.3	18.2	18.4	17.6	18.1	17.0	16.6	16.2	18.7	-	19.9	19.1
D$_2$ stage												
Brightness, %GE	87.5	88.5	89.0	89.9	86.6	87.2	88.0	89.2	88.6	88.2	89.1	89.5
Rev. brightness, %GE	84.4	86.2	86.4	87.6	83.2	84.1	85.4	86.4	86.2	85.1	86.9	87.1
Viscosity, cp	17.7	17.0	16.9	16.6	17.9	15.8	15.6	14.8	17.4	18.7	18.1	17.6

VII. Softwood ODE$_O$DED bleaching results

produced oxidized white liquor containing no sodium sulfide and greater than 90% conversion of the original sulfide to sodium sulfate.

- The Q-OWL has been shown to produce final pulp qualities as good as or better than those obtained with NaOH when used in oxygen delignification, extraction, and peroxide bleaching stages. These results were obtained on both hardwood and brownstock pulps and both in the laboratory and in the bleach plant.
- White liquor did not prove to be a satisfactory substitute for NaOH in any of the sequences examined. Both the brightness and viscosity values were lower when using WL than those obtained with either NaOH or the Q-OWL.

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	CAUSTIC SOURCE											
	NaOH				WL				Q-OWL			
	D, %											
Parameter	**0.8**	**1.0**	**1.2**	**1.4**	**0.8**	**1.0**	**1.2**	**1.4**	**0.8**	**1.0**	**1.2**	**1.4**
D_1 stage												
Brightness, %GE	81.6	81.4	82.5	83.8	80.7	82.4	83.3	84.6	82.3	83.0	85.0	86.3
Viscosity, cp	19.8	18.2	17.5	18.2	16.9	16.6	16.3	15.5	17.5	17.8	18.5	15.1
E_2 stage												
Brightness %GE	79.5	79.4	8.6	81.2	75.5	77.1	78.1	79.8	80.3	80.8	82.5	83.0
Viscosity, cp	17.4	17.4	17.1	16.3	16.6	15.7	16.0	14.5	17.5	16.6	17.0	15.9
D_2 stage												
Brightness, %GE	88.8	89.4	89.0	90.5	88.1	88.9	89.9	90.1	89.2	90.1	90.4	90.6
Rev. brightness, %GE	86.1	86.5	86.0	87.5	85.7	85.8	86.4	87.4	86.7	87.3	87.9	87.7
Viscosity, cp	16.4	16.2	16.3	15.9	16.0	15.8	15.1	14.6	16.8	17.1	15.0	15.9

VIII. Softwood $ODE_{OP}DED$ bleaching results

	CAUSTIC SOURCE		
Parameter	**NaOH**	**WL**	**Q-OWL**
Brightness, %GE	46.6	44.1	44.7
Viscosity, cp	21.9	16.4	17.9
Kappa no.	8.4	8.8	8.6

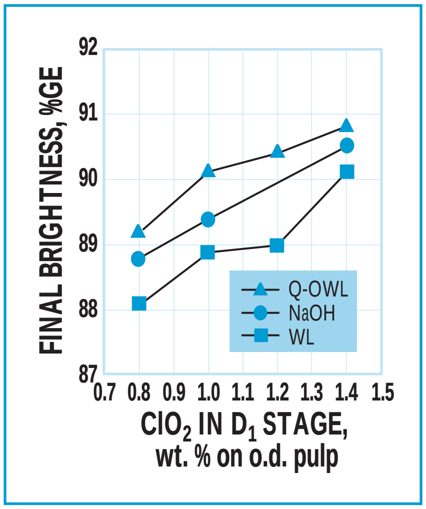
IX. Hardwood bleaching results after oxygen delignification stage

	E_O			E_{OP}		
	CAUSTIC SOURCE					
Parameter	**NaOH**	**WL**	**Q-OWL**	**NaOH**	**WL**	**Q-OWL**
Brightness, % GE	73.9	70.1	73.3	78.8	74.9	77.4
Viscosity, cp	17.0	14.8	16.5	14.7	14.1	16.9
Kappa no.	4.2	5.0	3.9	3.1	4.7	3.4

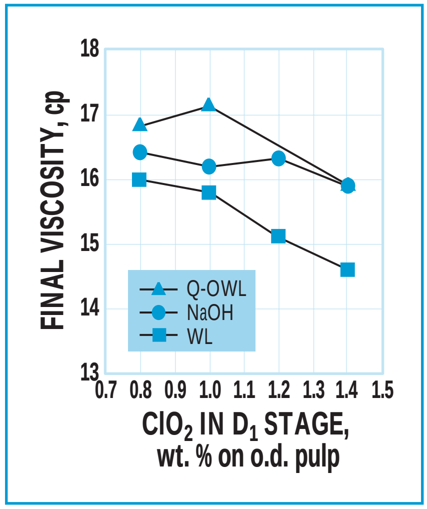
X. Hardwood bleaching results after ODE_O and ODE_{OP} stages

	ODE_OD			$ODE_{OP}D$			ODE_OP			$ODE_{OP}P$		
	CAUSTIC SOURCE											
	NaOH	**WL**	**Q-OWL**	**NaOH**	**WL**	**Q-OWL**	**NaOH**	**WL**	**Q-OWL**	**NaOH**	**WL**	**Q-OWL**
	D or P, %											
	0.8	**0.8**	**0.8**	**0.8**	**0.8**	**0.8**	**1.0**	**1.0**	**1.0**	**1.0**	**1.0**	**1.0**
Brightness, %GE	85.1	84.7	85.1	86.3	85.9	86.5	83.4	82.7	84.6	84.6	83.5	84.6
Viscosity, cp	16.1	13.9	16.0	13.6	13.1	16.1	13.2	11.2	15.0	11.9	12.4	14.3

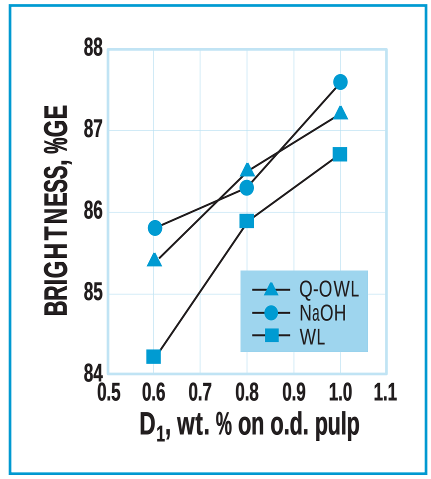
XI. Hardwood ODE_OD, $ODE_{OP}D$, ODE_OP, and $ODE_{OP}P$ results



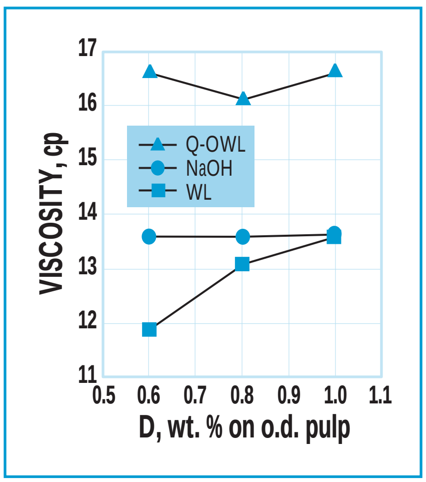
4. Softwood ODE$_{OP}$DED brightness vs. %D$_1$



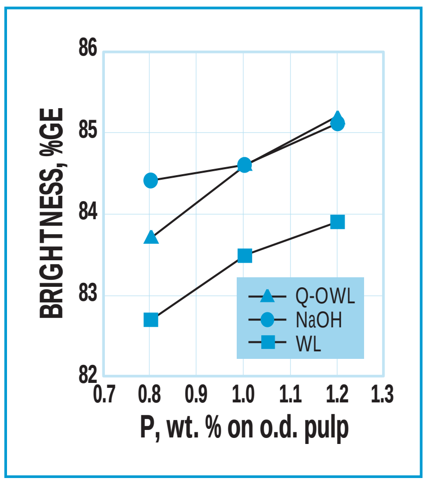
5. Softwood ODE$_{OP}$DED final viscosity vs. % D$_1$



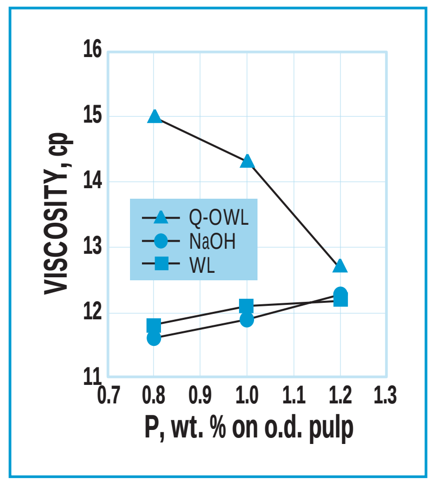
6. ODE$_{OP}$D sequence hardwood sample 2 brightness vs. D$_1$ charge



7. ODE$_{OP}$D sequence hardwood sample 2 final viscosity vs. D$_1$ charge



8. ODE$_{OP}$P sequence hardwood sample 2 brightness vs. D$_1$ charge



9. ODE$_{OP}$P sequence hardwood sample 2 viscosity vs. P charge

Caustic source	Pulp type	D$_2$, % ClO$_2$	D$_2$ brightness, %GE	D$_2$ viscosity, cp
NaOH	SW[a]	0.24	84.6	24.5
Q-OWL	SW	0.24	84.6	24.2
WL	SW	0.35	83.6	22.6
NaOH	HW[b]	0.22	87.0	24.2
Q-OWL	HW	0.20	86.9	24.4
WL	HW	0.32	86.0	22.9

[a]Softwood
[b]Hardwood

XII. Plant results–substitution in E$_2$ stage