Activation of alkaline peroxide delignification using a vanadium peroxo complex

MIRO SUCHY AND DIMITRIS S. ARGYROPOULOS

ABSTRACT

Transition metals have been used as additives in peroxide bleaching, mostly under acidic conditions. The effectiveness of such systems may be due to the in situ *formation of peroxometal complexes. To examine this hypothesis, we synthesized one of these compounds. We then examined its delignification efficiency by evaluating the reaction parameters and pulp properties.*

The effects of ammonium triperoxophenanthroline vanadate (ATPV) were examined under conditions compatible with conventional P-stage bleaching practices. Vanadium (V) peroxo complexes transfer oxygen to aromatic hydrocarbons at room temperature. The presence of 0.5% of APTV in the bleach liquor improved the delignification efficiency and pulp brightness. At this charge, the delignification efficiency of an activated P-stage is affected more by temperature than by retention time. Pulp viscosity was significantly reduced during the activated P-stage, but at the same kappa number, the viscosity values for an activated and a control pulp were approximately the same. This study demonstrated that transition metal peroxo complexes offer structural possibilities that have yet to be explored as active oxygen carrier compounds, with the possibility of regeneration.

Application:

A new class of transition metal complexes offers possibilities for the generation of new activators for peroxide and oxygen delignification.

HYDROGEN PEROXIDE HAS ALWAYS been a technologically attractive oxidant to the pulp and paper industry, with its significance becoming increasingly important as environmental regulations become more stringent. Beyond its ease of handling and application, hydrogen peroxide is also a versatile and benign compound whose decomposition products are water and oxygen. Among its major drawbacks are its high price, reduced selectivity, and its somewhat low efficiency compared to chlorine and chlorine dioxide. However, despite these drawbacks, recent accounts have shown that when using peroxide at high temperatures, the rate of reaction is significantly accelerated and the extent of lignin removal increases *(1)*. The combination of a high-temperature peroxide state (PH_T) with an ozone stage allows oxygen-delignified kraft pulp to be bleached up to a brightness level of 90 ISO *(2)*. High consistencies, high temperatures, and long retention times have also been claimed to assist delignification and brightness development during a P-stage *(3, 4)*. Production limitations imposed by longer retention times induced research which demonstrated that using higher pressures during a peroxide stage can significantly reduce the time required to reach a desired brightness level *(5)*.

Molecular oxygen has a triplet ground state whose direct interaction with singlet-state organic molecules is a spin-forbidden transition. This fact limits the oxidative selectivity of molecular oxygen. Industrially, it would be extremely beneficial to fix molecular oxygen within organic or inorganic compounds capable of transferring it selectively to an organic substrate such as lignin.

Peracids, such as Caro's acid, peracetic acid, and performic acid, can be considered as organic molecules containing active oxygen. In fact, they have all been shown to be effective delignification and bleaching agents *(6–9)*. An example of an inorganic molecule containing active oxygen is peroxymonosulfuric acid, which was shown to improve oxygen delignification of kraft pulps when used in two stages *(10)*. For all of these molecules, however, one may again cite high prices and reduced selectivity.

Dioxiranes also possess the ability to transfer a single activated oxygen atom onto aromatic and unsaturated substrates. As such, dimethyldioxirane (DMD) was tested as a novel and selective non-chlorine-containing bleaching agent for the production of fully bleached totally chlorine-free (TCF) pulp *(11)*. Detailed studies of the reactions of DMD with softwood lignin model compounds showed that the compounds' aromatic rings undergo *ortho* and *para* hydroxylation reactions, thus introducing new phenolic hydroxyl groups into the lignin structure *(12)*.

Another form of activated oxygen may also be present within peroxycarboximidic acid, which is thought to be an intermediate in the interaction of cyanamide with peroxide. For this reason, cyanamide has been proposed as a peroxide activator for bleaching sulfite pulps, with less success toward oxygen-delignified kraft pulps *(13, 14)*. However, recent research by Chen *et al.* *(15)* demonstrated that the dimeric form of cyanamide (dicyandiamide) is a con-

H_2O_2 charge*, %	NaOH charge*, %	$MgSO_4$ charge*, %	DTPA charge*, %
1	1.6	0.05	0.2
2	2.0	0.05	0.2
3	2.6	0.05	0.2
4	3.0	0.05	0.2
5	3.0	0.05	0.2

*Percentages based on ovendry pulp

I. Amounts of chemicals used for preparing bleaching solutions at different peroxide charges

siderably more effective activator of peroxide, allowing oxygen-treated pulps to be efficiently delignified.

Finally, the recent scientific and patent literature contains a number of examples where transition metals have been used as additives in peroxide bleaching, mostly under acidic conditions. Tungsten *(16)*, molybdenum *(17)*, silicomolybdates *(6, 18)*, and manganese complexes *(19)* have all been shown to offer significant benefits in this respect. Peroxometal complexes are known to be more efficient oxidants than hydrogen peroxide; these complexes are able to oxidize substrates such as alkenes, alcohols, ketones, and even aromatic and aliphatic hydrocarbons *(20)*. Therefore, it could be hypothesized that the effectiveness of such systems could be due to peroxometal complexes forming *in situ* when the transition metals interact with peroxide acting as oxygen transfer vehicles.

Compared to all the different systems enumerated herein, transition metal peroxy complexes offer a very large variety of structural possibilities that have yet to be explored as possible active oxygen carrier compounds (with the possibility of regeneration) for use by the pulp and paper industry. Prior to embarking on an extensive research program that will attempt to define structure–property relationships, we must examine the validity of the outlined hypothesis. For this purpose, we synthesized a representative member of this class of compounds and then examined in detail its efficiency toward activating peroxide delignification by paying particular attention to the various reaction parameters and product properties.

EXPERIMENTAL

Two oxygen-delignified kraft pulps (pine and hemlock) were used in these experiments. The kappa number of the pine pulp was 16.2, while that of the hemlock pulp was 17.2. The chelation (Q stage) was carried out at 1.6% consistency using a charge of 0.5% diaminetriethylenepentaacetic acid (DTPA) (on an ovendry basis) for 30 min at 50°C. The pulp was brought to the desired consistency using distilled and deionized water followed by acidification to pH 4.5 (with dilute sulfuric acid) prior to adding the chelant (in the form of a 4-g/L solution). Finally, the pulp was thoroughly washed with deionized water.

The activator $\{[NH_4][V(O\text{-}O)_3(phen)][H_2O]\}$ was prepared according to the procedure described by Sala-Pala and Guerchais *(21)*. Ammonium metavanadate, NH_4VO_3, (1.17 g, 0.01 mol) was dissolved in ice-cold 30% hydrogen peroxide (60 mL). A solution of phenanthroline monohydrate (1.98 g, 0.01 mol) in ethanol (200 mL) was added to the yellow solution. On standing at 0°C and, after about 12 hours, a yellow precipitate was formed. This precipitate was filtered, washed with cold ethanol, then ether and dried in a vacuum oven at room temperature for 24 hours. The compound does not have a sharp melting point but decomposes at approximately 100°C *(21)*. The identification of the synthesized compound was confirmed using infrared spectroscopy, which agreed with the spectra provided by Sala-Pala and Guerchais *(21)*.

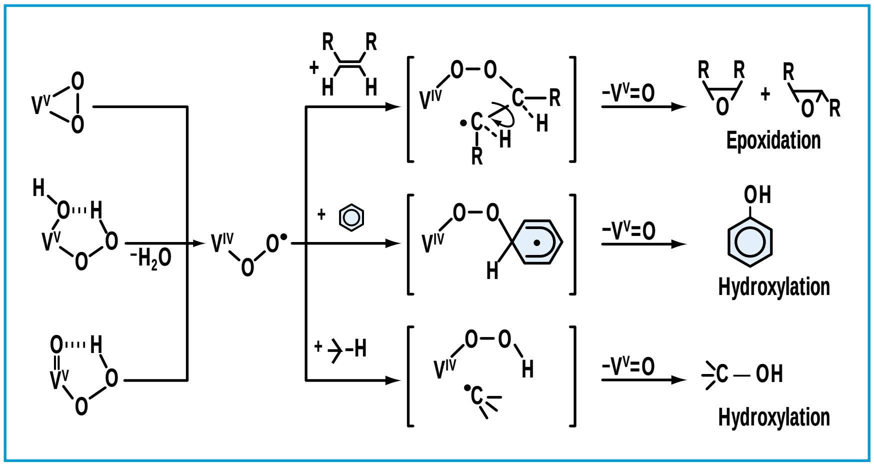
Peroxide bleaching (P-stage) was carried out at 10% consistency using a thermostated water bath maintained at 80 or 85°C. The composition of the bleach liquor used was as follows: 0.05% $MgSO_4$, 0.2% DTPA, and varying charges of H_2O_2 and NaOH (all expressed on an o.d. pulp basis). For activated bleaching, fresh solutions of ammonium triperoxophenanthroline vanadate (ATPV) were added to the bleach liquor in accordance with the required concentrations, as specified in the relevant figure captions. The chemicals (see **Table I**) were then mixed with the pulp, transferred into a polyethylene bag, and sealed. Thorough mixing was ensured prior to and during each bleaching experiment.

After each experiment, an aliquot of filtrate was collected and its pH was measured. Residual peroxide was also determined on a portion of the filtrate by determining the amount of iodine liberated from an acidified standard potassium iodide solution using a standardized 0.1*N* solution of sodium thiosulfate and a few drops of saturated ammonium molybdate indicator solution. The bleached pulp was finally diluted to 0.5% consistency, acidified to pH 4.5 with dilute sulfuric acid, and washed thoroughly with distilled water. Standard handsheets were then made, and brightness (Standard E.1), kappa number (Standard G.18), viscosity (Standard G.24P), and z-span tensile strength (Standard D.37P) measurements were carried out using standard CPPA procedures.

RESULTS AND DISCUSSION

A large number of synthetic procedures have been published describing well-defined transition-metal peroxides involving molybdenum, tungsten, and chromium, coordinated with a variety of ligands *(22, 23)*.

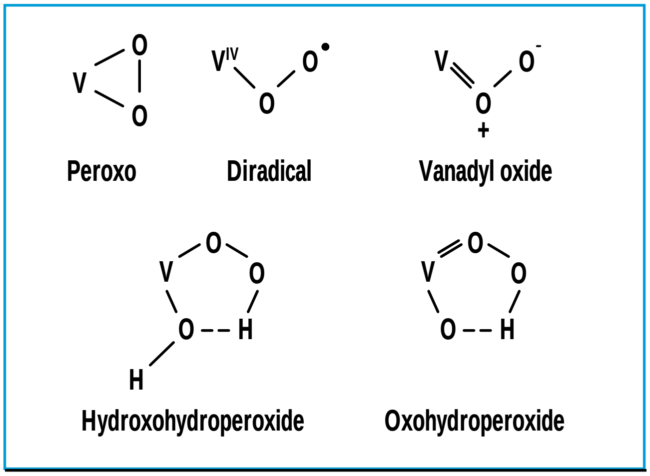
In contrast to previous efforts *(16–18)*, where tungstate and molybdate salts were used to promote peroxide *(16, 17)* and other bleaching processes *(18)* under acidic conditions, the present effort is focused at examining the effect of a vanadium peroxo complex, i.e., ATPV as an activator of the P-stage in the bleaching of oxygen-delignified kraft pulp under conditions compatible to conventional P-stage bleaching practices. ATPV is a water-soluble, stable yellow solid that can easily be prepared in a one-step synthesis.



1. Various possible active species that may be involved in the transfer of oxygen from the vanadium peroxo complexes to hydrocarbons **(24)**

One of the most striking features of vanadium (V) peroxo complexes is their ability to transfer oxygen to aromatic hydrocarbons at room temperature *(24)*. Toluene is readily hydroxylated by such complexes, yielding *o*- and *m*- creosols without the formation of coupling products. Peroxovanadium complexes also induce a variety of net two-electron oxidation reactions, causing the epoxidation and hydroxylation of alkenes and allylic alcohols and the oxidation of primary and secondary alcohols to aldehydes and ketones *(24, 25)*. The transfer of oxygen from the vanadium peroxo complexes to hydrocarbons is thought to occur via peroxo ring cleavage, yielding the vanadyl oxide or diradical species, or through the rearrangement of the intramolecularly hydrogen-bonded hydroxo-hydro-peroxide or oxo-hydro-peroxide molecules (**Fig. 1**).

Possible reaction mechanisms describing such epoxidation and hydroxylation reactions are shown in **Fig. 2.** Residual kraft lignin contains functionalities that are all amenable to oxidation by these reactions. More specifically, enol ethers are potential epoxidation sites, while the aromatic rings of lignin are amenable to hydroxylation. Finally, benzylic hydrogens may also be hydroxylated and then further oxidized to carbonyl groups. In the presence of hydroperoxide anions, carbonyl groups may then be rapidly reacted via the Dakin reaction, leading to side-chain scission within lignin.



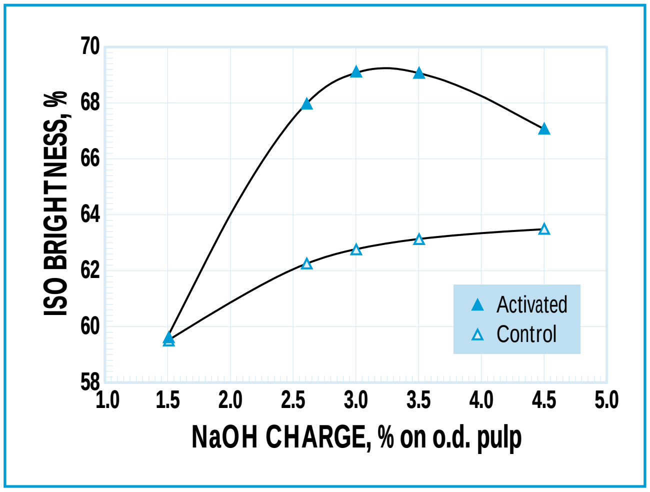
2. Epoxidation and hydroxylation reactions induced by the peroxo moieties of peroxovanadium complexes **(24)**

We therefore thought it appropriate to determine if such complexes could activate peroxide delignification of pulps of relatively low kappa number that have been depleted of phenolic hydroxyls. The oxygen-delignified pulp (kappa no. 16.2) was chosen to represent the worst-case scenario since its residual lignin is known to be depleted from phenolic hydroxyls *(26)* that, in general, augment the reactivity of the lignin.

Effect of alkali charge

Since the efficiency of an alkaline hydrogen peroxide bleaching stage is known to require optimum alkalinity that is specific to the type of pulp used [optimized in terms of brightness and delignification gains *(27–29)*], this variable was among the ones examined in conjunction with the activating system under examination. **Figure 3** compares the brightness gains obtained between the ATPV-activated peroxide stage and its control counterpart as a function of alkali charge. For the control experiments, an increase in the alkali charge from 1.5% to 2.6% caused a brightness increase of 2.7 points. For the same increase in alkalinity, however, 8.5 brightness points were gained when a 2% charge of the ATPV activator was used, with the maximum brightness gains being at 3% alkali.

Hydroperoxide anions are most likely the active nucleophiles during a peroxide brightening stage whose concentration depends on the alkalinity of the medium. However, alkalinity also affects the delignification efficiency of peroxide *(29)*. The enhanced brightness response apparent in the data of Fig. 3 for the activated peroxide experiments is most likely due to augmented oxidation reactions being caused within the



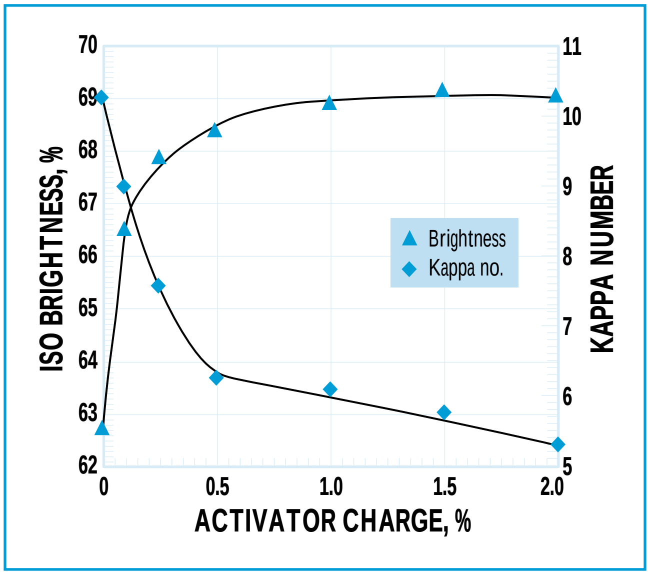
3. Effect of alkali charge on the brightness gains realized after a P-stage, for ATPV-activated and control runs. The experiments were carried out on chelated pine oxygen-delignified kraft pulp (kappa no. 16.2) at 80°C for 2 hours, using H_2O_2 and NaOH: 3%; activator charge: 2%; DTPA: 0.2%; and $MgSO_4$: 0.05%.

residual kraft lignin. This is evidenced by the fact that at a 3% alkali charge, the difference in kappa reduction between the activated and the control samples was 4 kappa units. This difference in lignin content was also reflected in the measured brightness gains.

Effect of activator charge

In our attempts (a) to further delve into the details of the observed activation and (b) at further optimizing the system under examination, the brightness and kappa number responses as a function of activator charge applied are plotted in **Fig. 4.** Using 3% peroxide and NaOH charges (optimum alkalinity as derived from Fig. 3), a marked increase in brightness was observed for activator charges up to about 0.5%. Higher activator charges resulted in only marginal brightness increases. These observations were also in agreement with the response of this pulp to delignification, i.e., the kappa number reductions observed. The fact that these two properties are so well correlated most likely signifies that the underlying process chemistries for brightening and delignification reactions are related *(29)*.

It is apparent that even small charges of activator present in the bleach liquors may cause significant improvements in both kappa number reduction and brightness gains compared to the control. More specifically, the presence of 0.2% of activator in the bleach liquors caused approximately 3 more points in kappa number reduction compared to its control counterpart. However, a level of 0.5% of activator seems to be optimal for delignification and brightness development. At this charge, the delignification efficiency of the peroxide stage is increased by at least 50% (Fig. 4). Activator charges exceeding the 0.5% level showed no significant improvement in kappa number reduction and brightness gains. This is most likely attributed to a lack of peroxide in the bleach liquor; the peroxide is essential for the activation process. Further experiments (to be discussed later) showed that additional delignification can be obtained at higher peroxide charges.



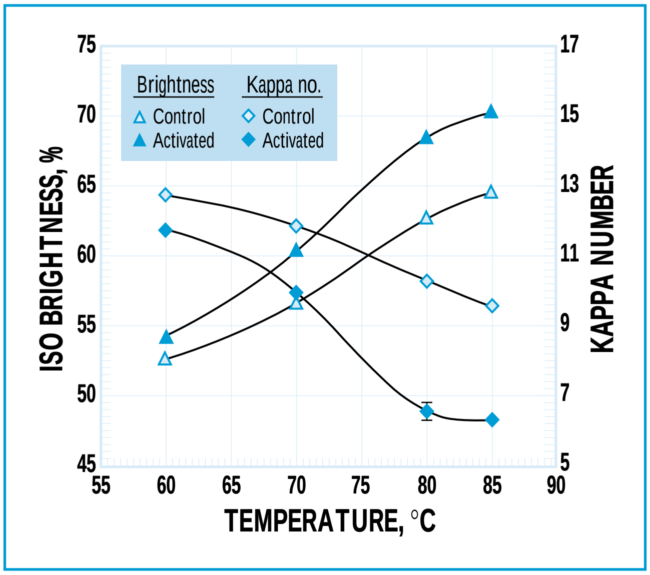
4. Effect of activator charge on brightness and kappa number for an oxygen-delignified pine kraft pulp (kappa no. 16.2). P-stage conditions: temp.: 80°C; retention time: 2 hours; H_2O_2 and NaOH: 3%; DTPA: 0.2%; and $MgSO_4$: 0.05%.

Effect of time and temperature

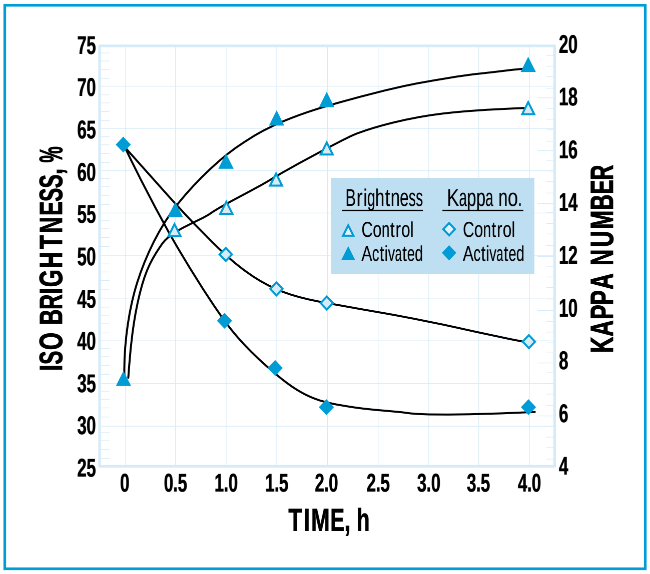
In general, peroxide delignification and bleaching require temperatures on the order of 90°C and require extended retention times *(3, 4, 30)*. At lower temperatures, peroxide reacts with the pulp to a very limited extent *(1)*. High temperatures and longer retention times force the peroxide to react with the pulp, causing lower kappa numbers and higher brightness levels. Therefore, the objective of any endeavor toward activating the P-stage is to increase the efficiency of the process and consequently decrease the temperature and/or the retention time required for a given level of delignification and brightening. Furthermore, efficient activation systems may also permit improved brightnesses and delignification levels to be obtained under conditions otherwise identical to those of peroxide-only bleaching.

In this study, the impact of the presence of activator toward brightness development and kappa number reduction was examined both as a function of temperature and time for a pine oxygen-delignified pulp at a specific (optimum) combination of peroxide and alkalinity (3%).

In accordance with previous research *(1, 2, 27)*, the brightness of the pulp after the P-stage was found to almost monotonically increase with temperature for both the control and the activated systems. The difference in brightness gains between activated and nonactivated stages became more pronounced as the tempera-



5. *Effect of temperature on the efficiency of activated and control P-stages toward brightness gains and kappa number reductions. P-stage conditions: H_2O_2 and NaOH: 3%; activator charge: 0.5%; DTPA: 0.2%; and $MgSO_4$: 0.05%. Bleaching time: 2 hours.*



6. *Effect of retention time on the efficiency of activated and control P-stages toward brightness gains and kappa number reduction. P-stage conditions: H_2O_2 and NaOH: 3%; activator charge: 0.5%; DTPA: 0.2%; and $MgSO_4$: 0.05%. Bleaching temp.: 80°C.*

ture was increased. For example, in the presence of the activator, 1.6 ISO points were gained at 60°C while 5.7 ISO points were gained at 80°C (**Fig. 5**).

Similarly, the efficiency of delignification (as reflected by kappa number measurements) was found to increase with increasing temperature. While for the control experiments, the kappa number reduction was nearly linear (Fig. 5), the effect of temperature was more dramatic toward enhancing delignification when the activator was used, especially at the temperature interval 70–80°C. At 80°C, the presence of the activator improved the kappa reduction by 4 points, while higher temperatures did not show further benefits.

As anticipated, an increase in retention time resulted in improved brightnesses and lower kappa numbers for both the activated and control P-stages. The development of brightness as a function of time was rather rapid during the first 2 hours of bleaching (**Fig. 6**). Activation was found to induce changes in the obtained brightness levels within 30 min, with the maximum effect (7.3 ISO units) observed at about 90 min.

Increased retention time also offered benefits toward reducing the kappa number of the P-stage, with these benefits being more significant when the P-stage was used in conjunction with 0.5% of ATPV. However, in view of the data shown in Fig. 5, the delignification efficiency of an activated P-stage seems to be affected somewhat more by temperature increases than by retention time increases. While retention time was found to have a uniform effect toward reducing the kappa number of the control pulps over a 4-hour period, the presence of the activator caused a rapid decrease in kappa number during the first 2 hours, with no further reduction thereafter.

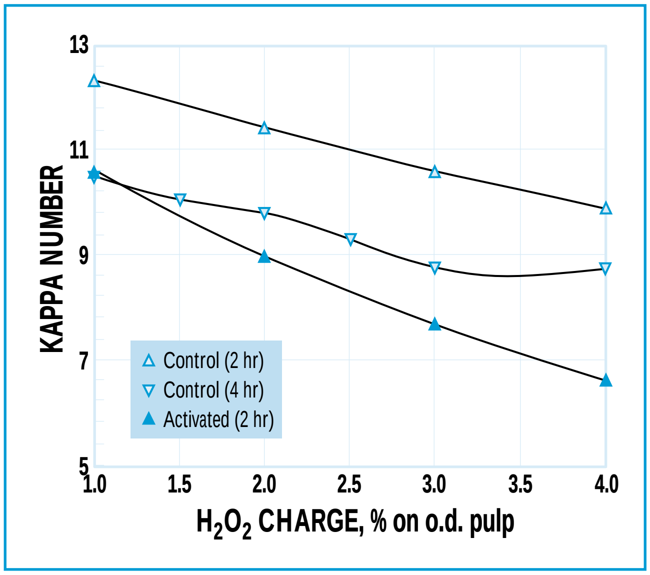
A closer examination of the combined data in Figs. 5 and 6 may now be summarized as follows: The brightness of an oxygen-delignified pine kraft pulp (kappa no. 16.2) may be increased by 5.7 ISO points when the pulp is bleached for 2 hours with activated peroxide (0.5% activator charge) at 80°C.

By adding 0.5% of ATPV into the peroxide bleach liquor and by carrying out the P-stage at 80°C for 2 hours, one obtains almost the same brightness gains as if the temperature of the P-stage were 85°C and the retention time were 4 hours. An additional 4 points in brightness gains may be achieved by extending the retention time of an activated P-stage to 4 hours at 80°C.

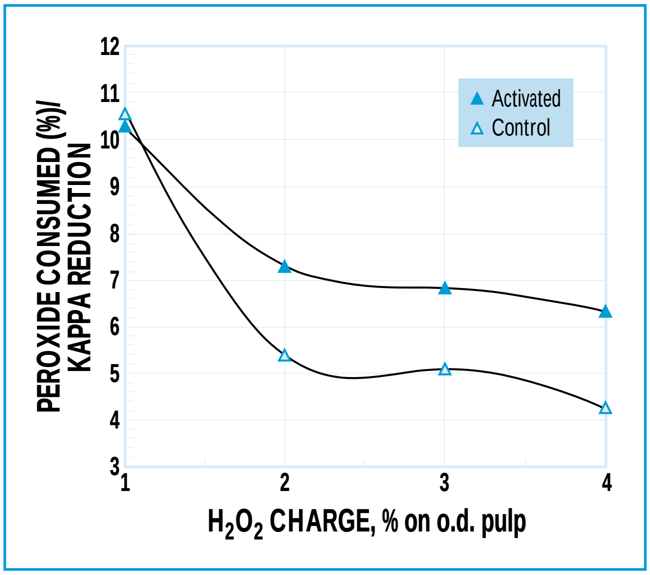
Effect of peroxide charge

A number of literature accounts *(7, 31)* claim brightness and delignification gains at elevated hydrogen peroxide charges. This variable (hydrogen peroxide charge) was also examined in detail during this effort. **Figure 7** shows the delignification efficiency of various activated and control P-stages as a function of peroxide charge at two retention times.

A relative insensitivity to the degree of delignification was observed when consecutively higher charges of peroxide were applied. For a 2-hour retention time, increasing the peroxide charge in the control experiments by 1% resulted in a reduction of 1 kappa unit (Fig. 7). A 4-hour retention time was no more beneficial, since delignification was practically stopped at about a 2.5% peroxide charge. At this point in the delignification regime, it is likely that most of the phenolic hydroxyl groups would have been eliminated from within the residual lignin. As such, condensed and possibly fully etherified lignin structures, which contain no reactive sites for the peroxide to react to, render the molecule inert toward further attack



7. Effect of peroxide charge on delignification efficiency for activated and control P-stages at two retention regimes. Bleaching conditions: temp.: 80°C; chemical charges per Table I; activator charge: 0.5%.



8. Peroxide consumed per kappa number reduction for a control and an activated series of bleach runs at various peroxide charges. Bleaching conditions: temp.: 80°C; retention time: 2 hours; chemical charges per Table I; activator charge: 0.5%.

and degradation *(17)*. This sequence of events, coupled with the fact that vanadium peroxo complexes have a demonstrated ability to transfer oxygen to aromatic hydrocarbons *(24)*, may be offered as a potential explanation for the improved delignification efficiency apparent in Fig. 7 for the ATPV-activated experiments at 2 hours of retention time. Consequently, the augmented delignification gains, as a function of peroxide charge, that are apparent in the activated experiments may imply that there is a relationship between hydroxyl groups introduced in lignin and peroxide charge. It is conceivable that at higher peroxide charges, the peroxide concentration is high enough to cause the regeneration of already-consumed activator molecules *(25)*.

For a hemlock pulp (kappa no. 17.5), in the absence of peroxide and in the presence of a 2% activator, approximately 2 kappa units of delignification were obtained with a concomitant increase in brightness of about 4 ISO points.

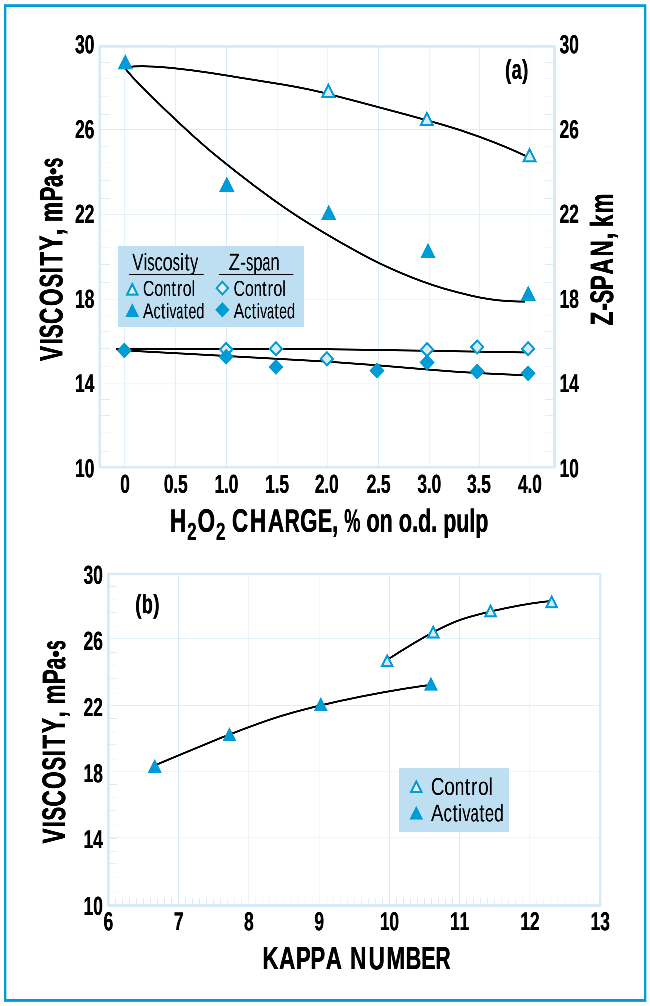
Despite the data of Fig. 7, where we show that the presence of the activator caused greater delignification at a given peroxide charge, **Fig. 8** shows that the presence of the activator invariably required more peroxide per kappa number reduction. However, this was not the case for the peroxide charge of 1%. At this charge, Fig. 7 showed that the presence of the activator caused an extra 2-kappa-unit reduction, while the peroxide consumption per kappa unit reduction was almost identical (Fig. 8). Beyond a peroxide charge of 1%, however, the peroxide consumption was always greater for the activated runs, possibly due to an oxidation reaction with the lignin that could not take place in the absence of the activator. It is thus logical to assume that lignin oxidation reactions that become possible only in the presence of the activator require more peroxide.

Pulp strength considerations (viscosity and zero-span tensile strength)

The selectivity of the studied P-stage was also examined by conducting pulp viscosity measurements. A significant loss in pulp viscosity is apparent when the activator was used, with these losses being augmented at higher peroxide charges [**Fig. 9(a)**] and at lower pulp kappa numbers [**Fig. 9(b)**]. Despite the viscosity drop apparent in the lower-kappa-number pulps, the zero-span tensile strength of the pulp is virtually unchanged when comparing the control to the activated stages. It is likely that the increased viscosity losses, which are apparent for the activated P-stage, are a consequence of increased delignification. Because the lower lignin contents are present in the pulp [Fig. 9(b)], the severity of radical attack on the cellulose is enhanced *(29, 30)*. Alternatively, the initial drop in viscosity may also be characteristic of the presence of the activator. Further detailed studies on the subject may offer more insight into the issue. The plots of pulp viscosity vs. kappa number [Fig. 9(b)] also show that the viscosity loss per kappa number drop is less pronounced in the activated P-stage.

Comparison with dicyandiamide

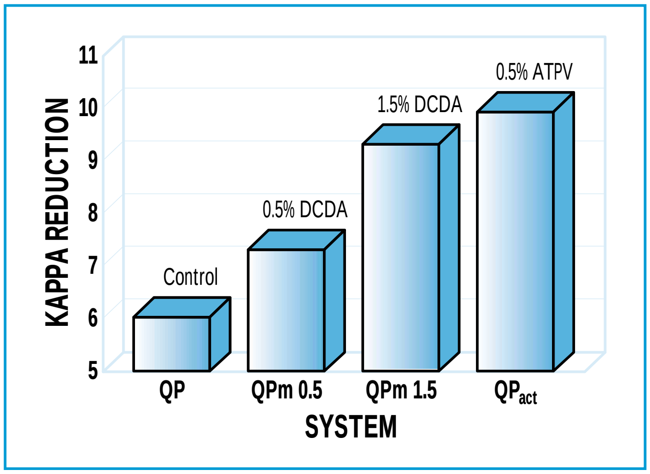
To further probe the process of peroxide activation with peroxy transition metal complexes, a comparison of their delignification efficiency was made with that of dicyandiamide (DCDA). This is because cyanamide, in the presence of alkaline hydrogen peroxide, is thought to induce the *in situ* formation of peroxycarboximidic acid *(13, 32)*,



9. (a) Viscosity and Z-span pulp tensile strength as a function of peroxide charge for a series of activated and control P-stages. (b) Pulp viscosity as a function of kappa number for the same series of activated and control P-stages. Bleaching conditions: temp.: 80°C; retention time: 2 hours; chemical charges per Table I; activator charge: 0.5%.

which is distinctly different than the structure of the metal-coordinated peroxy functionalities present in the transition metal complex under examination. This comparison was made on the same oxygen-delignified, pine kraft pulp of kappa no. 16.2, using two charges of DCDA (0.5% and 1.5%). The choice of all other variables was guided by the earlier work of Chen *(15)* and the optimization effort described so far. All activated systems showed improved delignification efficiencies, as measured by kappa number measurements, when compared to the control (**Fig. 10**). Furthermore, while the control experiments decreased the kappa number of the pulp by 6 units (37% delignification), using 0.5% ATPV reduced the kappa number of the same pulp, under otherwise identical conditions, by 9.9 kappa units (61% delignification).

At equivalent charges of activator (0.5%) and under otherwise identical process conditions, DCDA showed a somewhat lower delignification efficiency to that of ATPV. Using 1.5% of dicyandiamide afforded a similar delignification efficiency to that obtained when 0.5% APTV was used (Fig. 10).



10. A comparison of delignification efficiencies for three systems: (a) alkaline peroxide (P), (b) dicyandiamide (DCDA)–activated peroxide (Pm) at 0.5% and 1.5% charges, and (c) ammonium triperoxophenanthroline vanadate (ATPV)–activated peroxide (Pact) at 0.5% charge. All experiments were conducted on oxygen-delignified chelated (Q) pine kraft pulp (kappa no. 16.2). Other delignification conditions: temp.: 80°C; retention time: 2 hours; NaOH and H_2O_2 charges: 3%; DTPA: 0.2%; and $MgSO_4$: 0.05%.

Effect of ATPV peroxide activation on brightness response

The data in **Table II** show significant improvements in brightness gains for the activated peroxide stage, with the effect being augmented at higher peroxide charges. However, similar improvements were observed for the control P-stage when a longer retention time (4 hours) was used.

Moreover, the plot of brightness as a function of kappa number **(Fig. 11)** indicates that activated delignification does not contribute directly to brightness development. This is because the slopes for both the activated and the control P-stages are the same.

Effect of wood species

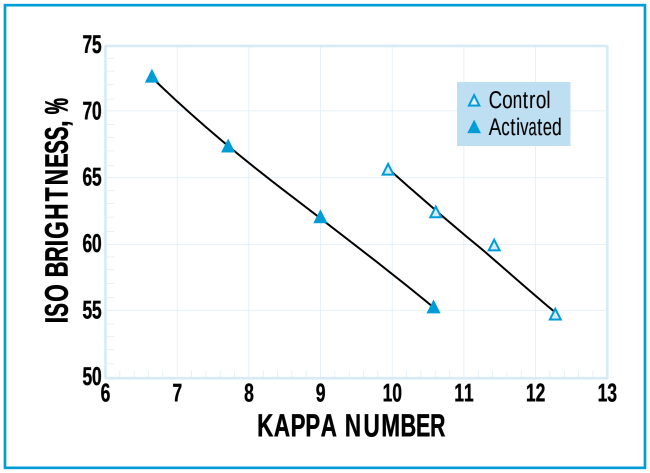
We concluded our preliminary investigation by examining the bleaching response of another wood species known to be relatively harder to bleach to full brightness compared to pine, i.e., an oxygen-delignified hemlock kraft pulp of kappa no. 17.5. **Table III** shows that despite the lower starting brightness (30.3 ISO), significant gains in both brightness and delignification were realized when the activator was present in the P-stage. Furthermore, the higher the peroxide charge, the greater the observed effect.

Even for the harder-to-bleach hemlock oxygen-delignified kraft pulp, peroxide activation by ATPV offers an increase in the delignification efficiency of the peroxide.

H_2O_2 charge, %	P 2 hours, ISO	P 4 hours, ISO	P_{act} 2 hours, ISO
1	54.8	58.9	55.3
2	60.0	64.5	62.1
3	62.5	67.5	67.5
4	65.7	70.0	72.6

*Ammonium triperoxophenanthroline vanadate

II. Brightness (ISO) measurements for pulps bleached with hydrogen peroxide at various peroxide charges and at two retention regimes in the presence and absence of the activator ATPV*



11. Comparative plots of pulp brightness vs. kappa number for activated and P-stages. Bleaching conditions: temp.: 80°C; retention time: 2 hours; activator charge: 0.5%; and other chemical charges per Table I.

H_2O_2 charge, %	BRIGHTNESS ISO, % Control	BRIGHTNESS ISO, % Activated	KAPPA NUMBER Control	KAPPA NUMBER Activated
1	45.3	45.6	12.9	11.8
2	50.1	54.8	11.3	8.8
3	53.0	59.5	10.2	7.1
4	57.8	66.2	9.6	5.8
5	58.0	66.8	9.4	5.5

*Initial pulp kappa no.=17.5, initial brightness=30.3 ISO, retention time=2 hours, temp.=80°C, alkali charges per Table I, activator charge=2%.

III. Data obtained for peroxide and activated peroxide bleaching of oxygen-delignified hemlock pulp at different peroxide charges*

CONCLUSIONS

Ammonium triperoxophenanthroline vanadate, when used as an activator to the P-stage in bleaching oxygen-delignified kraft pulps, offers significant improvements in the delignification efficiency and brightness of the pulp. Possible mechanisms for this activation could involve hydroxylation and epoxidation reactions that occur between the peroxide and the residual kraft lignin.

The optimum conditions for the use of the examined activator are as follows: activator charge: 0.5%; temp.: 80°C; retention time: 2 hours; and peroxide and alkali charges: 3%. However, at higher peroxide charges, the activator was found to perform even more efficiently. The optimum combination of alkali and peroxide needs to be determined for each individual pulp.

While the pulp viscosity was significantly reduced during the activated P-stage, this had a minor effect on the zero-span tensile strength of the resulting pulps. At the same kappa number, the viscosity values for an activated and a control pulp were approximately the same. The data imply that attempts to increase the extent of delignification by increasing the charge of peroxide may cause more severe viscosity losses when the system is not activated.

In general, this study has shown that transition metal peroxy complexes offer a very large variety of structural possibilities that have yet to be explored as possible active oxygen carrier compounds (with the possibility of regeneration) for use by the pulp and paper industry. TJ

Suchy is a visiting research student and Argyropoulos is a professor at PAPRICAN/ McGill University, Pulp and Paper Research Centre, Department of Chemistry, 3420 University St., Montreal, PQ H3A 2A7, Canada.

The authors would like to acknowledge Dr. R. M. Berry for providing constructive criticism during the writing of this paper. This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) in the form of a strategic grant.

Received for review June 30, 1998.

Accepted April 19, 1999.

LITERATURE CITED

1. Roy, B. P., Van Lierop, B., and Audet, A., *TAPPI 1995 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 771.
2. Van Lierop, B., Roy, B., Berry, R., *et al.*, *TAPPI 1996 International Pulp Bleaching Conference Proceedings*, TAPPI PRESS, Atlanta, p. 303.
3. Desprez, F., Devenyns, J., and Troughton, N. A., *TAPPI 1994 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 929.
4. Troughton, N. A., Desprez, F., and Devenyns, J., *TAPPI 1994 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 807.
5. Stromberg, B. and Szopinski, R., *1994 International Pulp Bleaching Conference Proceedings*, CPPA, Montreal, p. 199.
6. Jakara, J., Paren, A., and Patola, J., *8th International Symposium on Wood and Pulping Chemistry*, K. C. L., Jyvaskyla, Sweden, 1995, p. 377.
7. Geng, Z. P., Chang, H-M., Jameel, H., *et al.*, *TAPPI 1993 Pulping Conference Proceedings*, TAPPI PRESS, Atlanta, p. 353.

8. Bailey, C. W. and Dence, C. W., *Tappi* 49(1): 9(1966).
9. Poppius, K., Laamanen, L., Sundquist, J., *et al., Paperi Puu* 2: 89(1986).
10. Allison, R. and Lachenal, D., *TAPPI 1994 Pulping Conference Proceedings,* TAPPI PRESS, Atlanta, p. 521.
11. Lee, C.-L., Murray, R. W., and Hunt, K., PCT patent application, Intern. Publication No. WO 92/13993 (Aug. 20, 1992).
12. Argyropoulos, D. S., Sun, Y., Berry, R., *et al., J. Pulp Paper Sci.* 22(3): 84(1996).
13. Sturm, W. and Kuchler, J. G., *Non-Chlorine Bleaching Conference Proceedings,* Miller Freeman, San Francisco, 1993, Paper no. 31, and DE pat. 4,004,364 (Feb. 13, 1990).
14. Chen, J. and Lee, C.-L., *Pulp and Paper Report 1093,* June 1994.
15. Chen, J., *Pulp and Paper Report 1169,* July 1995.
16. Eckert R. C., CA pat. 1,129,161 (Aug. 10, 1982).
17. Kubelka, V., Francis, R. C., and Dence, C. W., *J. Pulp Paper Sci.* 18(3): 108(1992).
18. Kakara, J., Paren, A., Patola, J., *et al., Paperi Puu* 76(9): 559(1994).
19. Mielisch, H.-J., Kordsachia, O., and Patt, R., *Papier* 50(10A Suppl. S): V16(1996) and *Proceedings of the 5th Brazilian Symposium on the Chemistry of Lignins and Other Wood Components,* Curitiba, PR, 1997, p. 44.
20. Jacobson, S. E., Muccigrosso, D. A., and Mares, F., *J. Org. Chem.* 44(6): 921(1979).
21. Sala-Pala, J. and Guerchais, J. E., *J. Am. Chem. Soc. A* 9: 1132(1971).
22. Connor, J. A. and Ebsworth, E. A. V., *Adv. Inorg. Chem. Radiochem.* 6: 279(1964).
23. Dickman, M. H. and Pope, M. T., *Chem. Rev.* 94(3): 569(1994).
24. Mimoun, H., Saussine, L., Daire, E., *et al., J. Am. Chem. Soc.* 105(10): 3101(1983).
25. Butler, A., Clague, M. J., and Meister, G. E., *Chem. Rev.* 94(3): 625(1994).
26. Sun, Y. and Argyropoulos, D. S. A., *J. Pulp Paper Sci.* 21(6): 185(1995).
27. Van Lierop, B., Berry, R. M., and Roy, B. P., *Proceedings of the 82nd Annual Meeting of the Technical Section,* CPPA, Montreal, 1996, p. 247.
28. Lachenal, D. and Papadopoulos, J., *Cellulose Chem. Technol.* 22(5): 537(1988).
29. Gellerstedt, G. and Pettersson, I., *J. Wood Chem. Tech.* 2(3): 231(1982).
30. Stevens, J. A. and Hsieh, J. S., *TAPPI 1995 Pulping Conference Proceedings,* TAPPI PRESS, Atlanta, p. 421.
31. Andrews, D. H. and Singh, R. P. in *The Bleaching of the Pulp: A Project of the Pulp Bleaching Committee,* TAPPI Pulp Manufacture Division, TAPPI PRESS, Atlanta, 1979, p. 211.
32. Hammer, B., Michaud, H., and Weiss, S., U.S. pat. 5,034,096 (July 23, 1991).