

# Emerging Bleaching Technologies

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## Abstract

The rapid pace of development of chemical pulp bleaching technology seen during the last decade appears to be continuing unabated. It has been driven by growing concern for the environment, as reflected in market pressure and increasingly stringent government regulation, forces which continue to play a prominent role in the industry's technology selection decisions. This paper briefly reviews recent developments in oxygen delignification, ECF bleaching, effects of pulping on bleachability, ozone delignification, catalyzed and activated hydrogen peroxide delignification, polyoxometalate delignification, enzyme applications and hexeneuronic acid removal.

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It is apparent to even the casual observer that kraft pulp bleaching technology has undergone remarkable changes during the last decade, and that the pace of the change remains high. Although the trends that led to these changes were apparent before the middle of the 1980's, it was then that the discovery of dioxins downstream of pulp mills set the industry on an irreversible path toward a transformation of its bleaching technology. First market demands and then regulations forced mills to adopt measures that would decrease discharges of chlorinated organic materials. AOX took its place alongside BOD, color and TSS as an effluent parameter to be closely monitored, and chlorine bleaching was marked for extinction. The growth of oxygen delignification intensified, mills learned how to use chlorine dioxide to replace all of the chlorine in the chlorination stage, and peroxide appeared in many more bleach plants than it had in the past. Ozone made its debut in 1992, and enzymes followed shortly thereafter. Compounds previously unknown by the industry suddenly became worthy of consideration as future bleaching agents -- dioxiranes, polyoxometalates, peracids. All of these technologies continue to evolve, becoming established, assuming new forms or getting closer to commercialization. This paper will review some of the more recent developments in each of these technology areas.

## Oxygen Delignification

Oxygen delignification (also referred to as "oxygen bleaching") can be defined as the use of pressurized oxygen and alkali to remove a substantial fraction, usually 35-60%, of the lignin in unbleached pulp. The benefits derive from the fact that both the chemicals applied to the pulp and the materials removed from the pulp are compatible with the kraft chemical recovery system. This enables the recycling of oxygen stage effluent to the recovery system by way of the brownstock washers, decreasing the potential environmental impact of the bleach plant. The decrease is roughly proportional to the amount of delignification achieved in the oxygen stage. This applies not only to

chlorinated organic byproducts, but also to other environmental parameters associated with bleach plant effluents, including BOD, COD and color.

After a period of slow growth, the industrial application of oxygen bleaching has expanded rapidly. The first commercial system was started in 1970 and total world capacity in 1980 was only about 10,000 tons per day. By 1992 the number of operating systems stood at more than 155, with a total capacity of more than 100,000 tons/day. By 1996, capacity had risen to 160,000 tons/day, as illustrated in Fig. 1 (1). Growth is likely to continue. As trends away from the use of chlorine and chlorine-containing compounds intensify, both technical and economic considerations will mandate the use of oxygen.

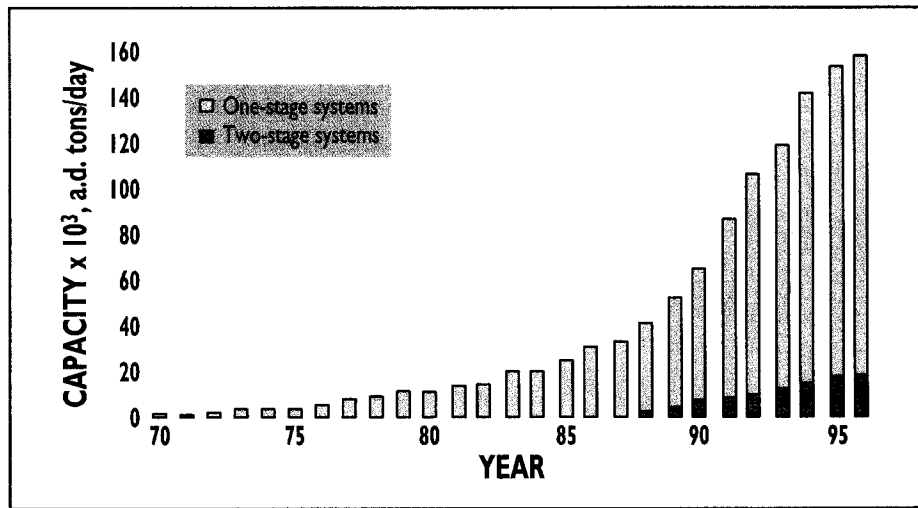
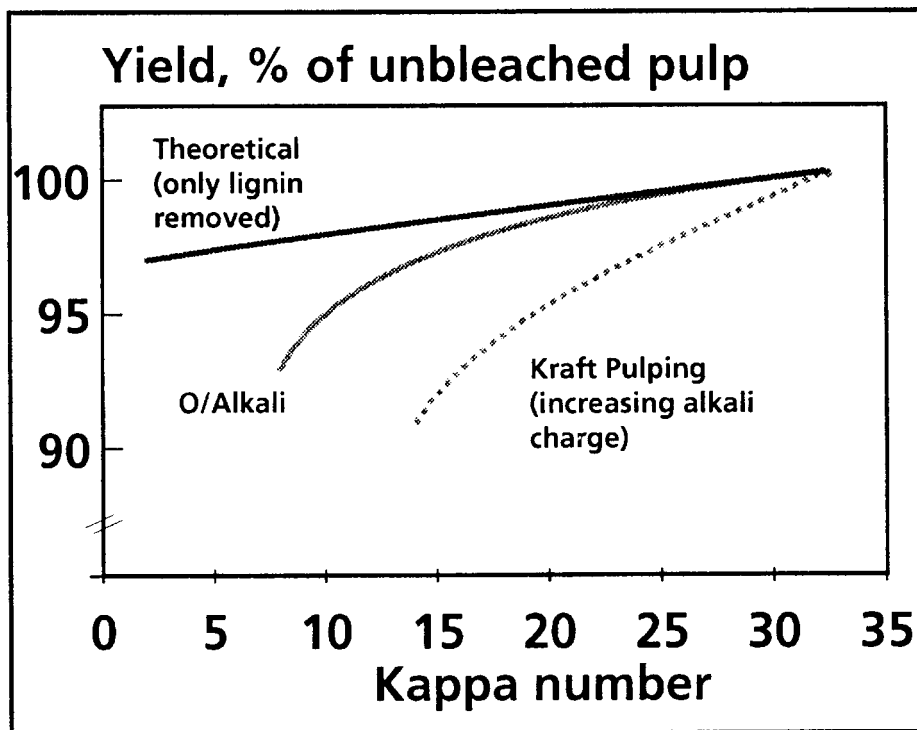


Figure 1. Growth of world oxygen delignification capacity (1)

Recent progress in the further development of oxygen delignification technology has centered on the evolution of two-stage systems for increased degrees of delignification. One of the drivers for this is the desire to increase pulp yield by terminating the kraft cook at a higher than normal kappa number and using the more selective oxygen stage to complete the delignification to kappa numbers at which other bleaching agents can take over. This is exemplified by the work of Bökstrom and Nordén, as reported at the 1998 International Pulp Bleaching Conference (2). Figure 2 illustrates the superior selectivity of oxygen delignification relative to that of kraft pulping. This figure also implies that oxygen is capable of removing 70-80% of the lignin in the unbleached pulp. This is not true for single-stage oxygen delignification. Medium consistency systems are seldom capable of reducing the kappa number by more than 40%, and even high consistency systems are limited to little more than about 50% delignification. Two stage systems have been installed at many mills to overcome these limitations while at same time retaining the selectivity needed for delignifying high kappa kraft pulps.



**Figure 2. Illustration of superiority of oxygen delignification selectivity over kraft pulping selectivity at low kappa numbers (2).**

Meanwhile, research has continued to make such systems even more selective and extensive. Figure 3, for example, shows the effect of independently varying the oxygen pressure in the two stages. The combination of high pressure in the first stage and low pressure in the second gives better selectivity than any of the other three possible combinations. This is part of a strategy based on choosing conditions for the first stage that are appropriate for the initial, rapid phase of delignification, and conditions for the second stage that are suitable for the second, slow phase of delignification. Thus, the first stage employs a small reactor with a correspondingly short retention time, a high oxygen pressure and a relatively low temperature. The second stage provides the long time and high temperature needed for the slow diffusion of lignin that is presumed to occur here, while keeping the alkali concentration low to minimize cellulose degradation. Interstage oxygen and alkali addition are not consistent with this concept, and are not recommended. Interstage washing improves selectivity, but is not required. These conditions result in good yield selectivity, as shown in Figure 4. Figure 5 illustrates the two-stage system incorporating these conditions.

### **Chlorine Dioxide Delignification**

Environmental pressures have caused a strong movement away from bleaching with molecular chlorine. The most readily implemented alternative is to replace all of the chlorine with chlorine dioxide. This has come to be known as "elemental chlorine-free" or ECF bleaching. The alternative, complete elimination of any chlorine-containing

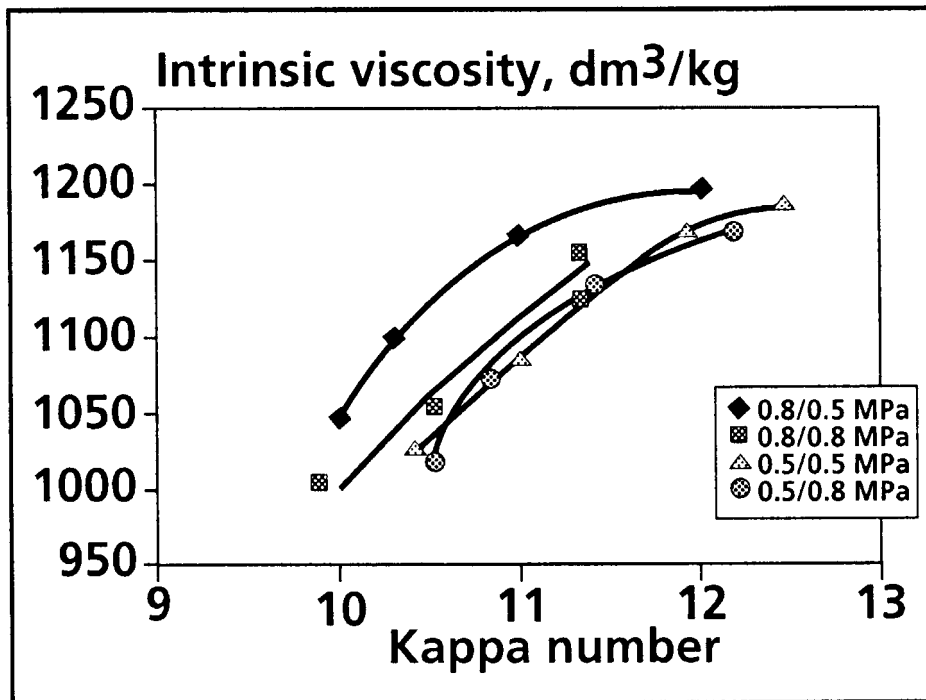


Figure 3. Effect of oxygen pressure in the first and second stage of two-stage oxygen delignification. Stage 1: 90°C; Stage 2: 120°C (2).

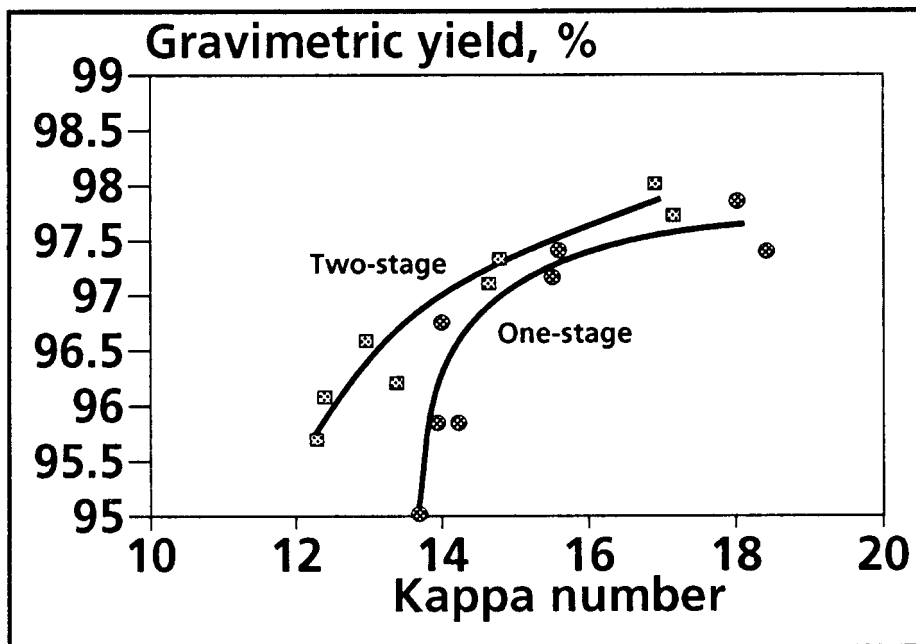
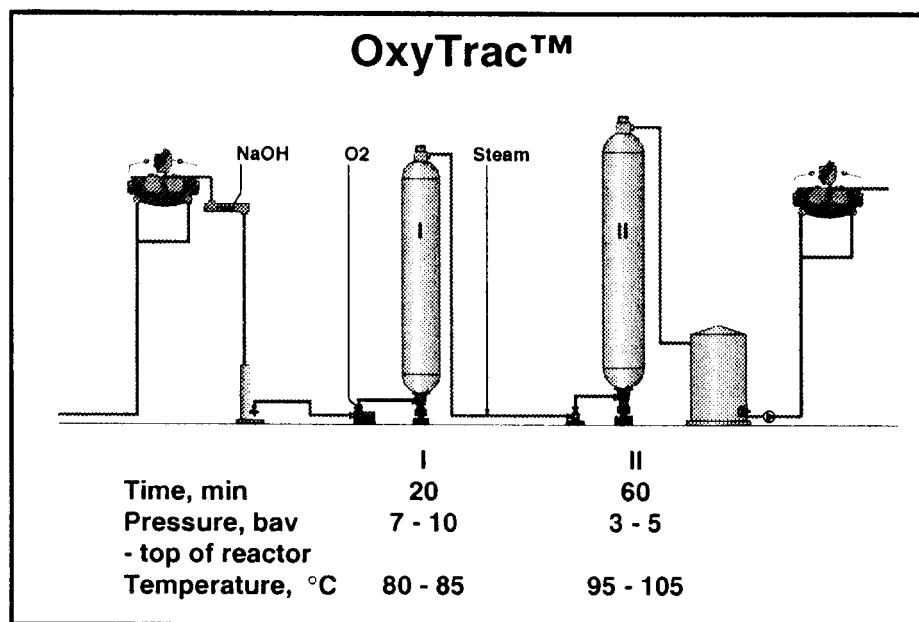


Figure 4. Yield after one- and two-stage oxygen delignification of softwood kraft pulp with kappa number 32.8 (2).



**Figure 5. A two-stage oxygen delignification system (2).**

compounds from the bleaching sequence, is known as “totally chlorine-free” (TCF) bleaching. The rapidity with which ECF technology is being implemented is readily apparent in the bleached chemical pulp (BCP) production statistics for several countries (3). In the United States, ECF bleaching accounted for approximately 33% of BCP production in 1994, rising to 57% in 1998. The corresponding figures for Canada are 50% and 76%, and for the world, 36% and 54%.

Before 1980, substitution of chlorine dioxide for chlorine in the chlorination stage was limited to 5-10%, and was practiced mainly to prevent losses in pulp viscosity and strength. In 1963 Rapson (4) reported that mixtures of chlorine and chlorine dioxide reacted synergistically to delignify pulp more effectively than equivalent amounts of either one alone, paving the way for the commercial use of higher substitution levels. A lack of economic or other incentives initially slowed the adoption of high levels of substitution, but this changed with the discovery that dioxins are a byproduct of chlorine bleaching and the impending regulation of AOX, for example by the USEPA’s Cluster Rule. Chlorine dioxide bleaching does not generate detectable levels of dioxin and produces far less AOX than chlorine bleaching. Chlorine reacts with residual lignin by pathways involving both substitution of chlorine for aromatic hydrogen atoms and oxidation. On the other hand, chlorine dioxide is primarily an oxidant and only indirectly leads to substitution through the formation of byproduct hypochlorous acid. The formation of tri-, tetra- and pentachlorinated phenolic compounds is virtually eliminated, as indicated by the absence of detectable amounts of such compounds after chlorine dioxide delignification. Chloroform formation is also suppressed, decreasing linearly with increasing substitution. Values of the order of 10 g/t have been observed when only chlorine dioxide is used.. Acute toxicity is eliminated and there is evidence that chlorine dioxide substitution decreases biological effects (5). BOD and COD are slightly decreased and color is substantially decreased, the reduction being of the order of 50%

relative to the case where only chlorine is used. Some chlorate, potentially toxic to plant life, is formed but is readily controlled by biological treatment or sulfur dioxide addition.

A recent development is the introduction of “Rapid  $D_0^R$ ” bleaching, in which the chlorine dioxide stage is conducted with a retention time so short (60-120 seconds) that the bleaching tower normally required for this stage can be completely dispensed with, a simple retention tube or pipe section being substituted. This requires only that the temperature be maintained at 50°C or higher and that good mixing be provided at the point of chlorine dioxide addition to the brownstock. Addition of an antichlor such as sodium sulfite or caustic may be required to consume the small amount of residual chemical that remains. The data in Table 1 show that the reaction is virtually complete in a very short time. Table 2 shows that the  $D_0^R$  stage performs almost as well as a  $D_0$  stage 30 times as long. An additional advantage of the  $D_0^R$  stage is that less AOX is generated than in a conventional stage, presumably because little time is available for secondary AOX forming reactions to occur.

**Table 1.  $D_0^R$ (EPO) Delignification of Kappa No. 29 Softwood and Kappa No. 15 Hardwood Kraft Pulps at 0.15 Kappa Factor with  $Na_2SO_3$  as Antichlor after  $D_0^R$**

|                               | Softwood |      | Hardwood |      |
|-------------------------------|----------|------|----------|------|
| $D_0^R$ time, sec             | 60       | 240  | 60       | 240  |
| $ClO_2$ consumed, %           | 98.6     | 99.6 | 94.4     | 99.5 |
| $D_0^R$ (EPO) brightness, ISO | 56.2     | 56.8 | 69.4     | 71.6 |
| $D_0^R$ (EPO) kappa no.       | 6.6      | 6.3  | 6.1      | 5.9  |
| $\Delta$ kappa/TAC            | 5.23     | 5.24 | 4.21     | 4.09 |

**Table 2.  $D_0^R$ (EPO) and  $D_0$ (EPO) Delignification of Kappa 29 Softwood and Kappa 15 Hardwood Kraft Pulps at 0.15 Kappa Factor with NaOH as Antichlor after  $D_0^R$**

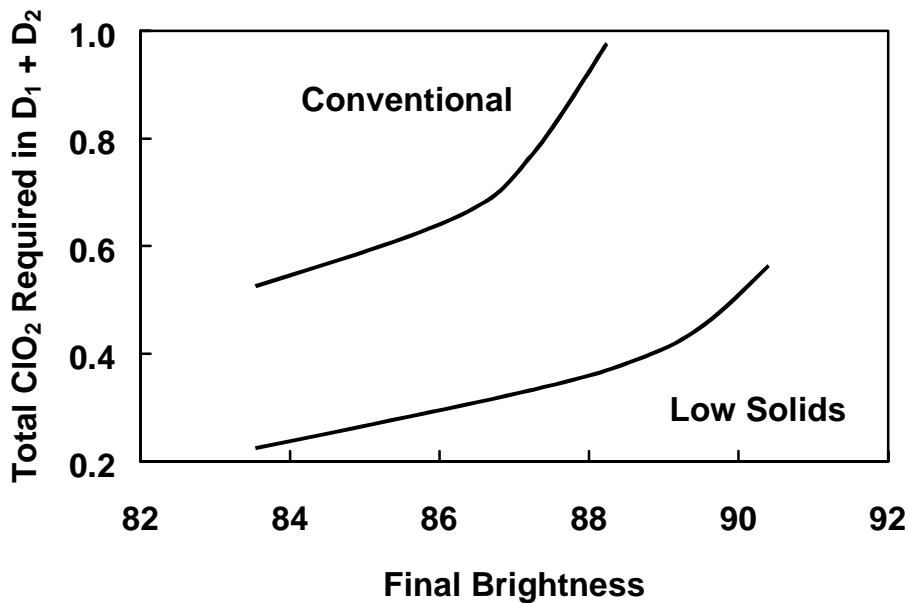
|                               | Softwood |      | Hardwood |      |
|-------------------------------|----------|------|----------|------|
| $D_0^R$ time, sec             | 60       | 1800 | 60       | 1800 |
| $D_0^R$ (EPO) brightness, ISO | 52.8     | 58.0 | 69.7     | 71.9 |
| $D_0^R$ (EPO) kappa no.       | 5.9      | 5.3  | 5.8      | 5.3  |
| Delignification, %            | 80       | 82   | 62       | 65   |

The  $D_0^R$  stage is a low capital cost alternative to the installation of a conventional, long retention time stage. Its availability also increases the number of options available to mills that must reconfigure their chlorine-based bleach lines to comply with the new AOX regulations. For example, a  $D_0^R$  stage could be added in an existing (C+D)(EO)D three stage bleach plant to convert the sequence to a  $D_0^R$ (EO)(D/E/D) virtual five stage sequence. This would only require the addition of 2 mixers and 2 retention tubes, including a mixer and retention tube for the short  $E_2$  stage. Very recent work in our

laboratory (6) has shown that conversion of a D(EPO)D bleach plant to the  $D_0^R$ (EPO)(D/E/D) sequence allows high brightnesses to be reached with significantly less chlorine dioxide and generates less AOX..

Another option is to eliminate washing between the  $D_0^R$  and (EO) stages. This would give the  $D_0^R$  stage a very large capital cost advantage over the conventional  $D_0$  stage. In addition, it would sharply reduce the AOX output of the bleach plant, since most of the AOX in the  $D_0$  filtrate carried into the (EO) stage would be destroyed by alkaline hydrolysis (7). These benefits would, of course, have to be weighed against the increase in caustic charge that would be needed in the (EO) stage, but that increase would be moderate because chlorine dioxide, in contrast to chlorine, generates only moderate amounts of acidic products. Eliminating the  $D_0$  washer would also offer the additional possibility for reconfiguring existing bleach plants of using the existing C stage washer to decrease chlorine dioxide requirements by washing before the final D stage. Thus an existing (C+D)(EO)D three stage bleach plant sequence would be converted to a ( $D_0^R$ /EO)(D/E)D sequence with extremely low AOX and lower chlorine dioxide requirement than if the former (C+D) washer were used between the  $D_0^R$  and (EO) stages.

Other recent work in our laboratories has investigated the effects of digester conditions on pulp bleachability. In some cases these effects can be substantial, as shown by a comparison of the bleachability of kraft pulps with pulps produced in kraft cooks where the time profiles of the concentrations of alkali, hydrosulfide and dissolved organic material (8) were controlled (“Low Solids” cooks). Figure 6 illustrates the magnitude of the differences observed in that study. At high brightness levels, the differences in brightening stage  $ClO_2$  requirements can be as high as 60%.



**Figure 6. Minimum total  $ClO_2$  requirement in the  $D_1+D_2$  stages for low-solids and control hardwood pulps.**

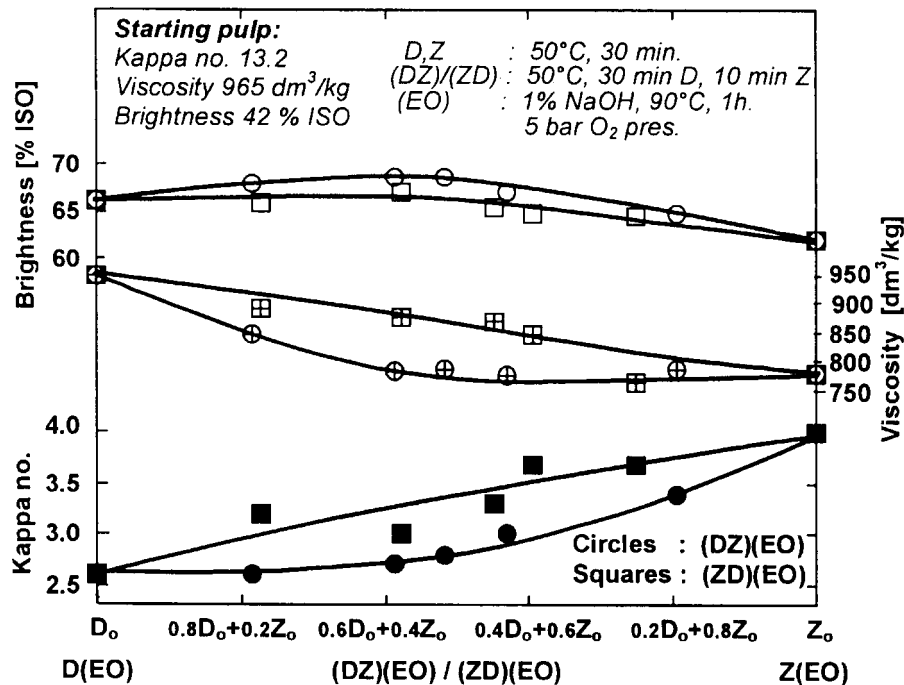
## Ozone Delignification

Ozone is a vigorous oxidizing agent that is capable of extensively removing the residual lignin in kraft pulp but which, by virtue of its extreme reactivity, also has the potential to damage cellulose and decrease pulp strength. This and other obstacles, including its very low solubility in water, prevented its commercial use for pulp bleaching for many years after the discovery that it could effectively bleach kraft pulp (9). In the late 1980's, however, increasingly stringent effluent quality demands provided the driving force for pilot-scale development. The first commercial use of ozone to bleach kraft pulp took place at the Union Camp Mill in Franklin, Virginia in 1992 (10). In October, 1998, there were reported to be a total of 20 ozone bleaching stages in commercial operation (11). A recent survey of Nordic mills identified six ozone stages in the 22 responding mills (12). Commercial ozone (Z) stages include both medium consistency and high consistency applications in both TCF and ECF sequences.

Among recent developments in the area of ozone bleaching technology is the use of ozone and chlorine dioxide in the same bleaching stage. The resulting (D/Z) and (Z/D) stages have the advantage of using much of the existing low consistency bleach plant equipment and are quite selective when the ozone charge is limited to reasonable levels. This approach allows the amount of chlorine dioxide in the delignification stage to be reduced, which has the beneficial effect of reducing AOX generation. More importantly, however, it may allow some mills to reach their effluent quality targets without installing new chlorine dioxide generation capacity. This method of using ozone has been the subject of several recent studies, including one by Toven (13). Figure 7, taken from that study, shows the results of experiments in which the chlorine dioxide in a D(EO) sequence was progressively replaced with ozone at the rate of 0.7 kg ozone per kg chlorine dioxide. When no ozone was used the chlorine dioxide charge was 0.95%. It is apparent from the kappa numbers at the extremes of the figure that this replacement ratio results in less effective delignification by ozone than by chlorine dioxide. For equal efficiency more than 0.7 kg would have been necessary to replace 1 kg chlorine dioxide. It should be noted that there is some disagreement in the literature on this point, since at least one other study found that less ozone was needed (14). The (D/Z) order was better than (Z/D). Figure 7 also shows that (D/Z) bleaching exhibits a synergistic effect, combinations giving lower kappa numbers than would be expected on the basis of those obtained with either bleaching agent alone.

## Delignification with Hydrogen Peroxide and Related Compounds

Alkaline hydrogen peroxide has long been known as an effective brightening agent for use in the latter part of chemical pulp bleaching sequences, where it is particularly effective for imparting brightness stability to the bleached pulp. Its use as a delignifying agent is more recent, however, having been commercialized in the late 1970's (15). More recently, its delignifying power has been increasingly utilized in bleaching sequences designed for improved effluent quality.



**Figure 7. Bleaching with combinations of ozone and chlorine dioxide in the same stage, followed by oxygen reinforced alkali extraction. Filled symbols: kappa number. Partially filled symbols: viscosity. Open symbols: brightness. Circles: (D/Z)(EO). Squares: (Z/D)(EO) (13)**

A most important aspect of any use of hydrogen peroxide for pulp bleaching is the role of trace amounts of transition metal ions, particularly iron, manganese and copper. Their main effect is to catalyze the decomposition of hydrogen peroxide, which normally results in a waste of peroxide and a diminished bleaching effect. The viability of peroxide as a delignifying agent only became established when technology was developed for efficiently controlling the detrimental effects of trace metals. This technology relies on the use of chelating agents under judiciously chosen conditions of pH, time and temperature to remove transition metals, particularly manganese, while only partially removing alkaline earth metals, particularly magnesium, which exert a protective effect, decreasing peroxide decomposition (16). Such a chelation step, known as a “Q” stage, allows the conditions in the succeeding peroxide stage to be made more severe, a necessary step in overcoming the sluggishness of the reaction of hydrogen peroxide with lignin under milder conditions. Typical conditions vary from 4 hours at 90°C to a few minutes at 120°C. The resulting QP sequence has been called the Lignox Process and is capable of 40-60 % delignification. In existing installations, it is applied to oxygen delignified pulp. Its effectiveness may be further enhanced by pressurization with oxygen. The resulting “pressurized peroxide” or (PO) stage has been extensively commercialized in Scandinavia, where a survey found that 10 of 45 bleach lines employed a (PO) stage (12). Most of these were TCF lines.

Although removal of metal ions from peroxide bleaching systems is generally beneficial, because it decreases the rate of metal-catalyzed peroxide decomposition, it appears that traces of metal ions are needed for bleaching to occur. This is strongly suggested by experiments with simple compounds that are structurally similar to lignin. Such compounds are unaffected by hydrogen peroxide when metal ions are virtually absent, but are destroyed by peroxide in the presence of certain metal ions. This phenomenon has led to the development of metal ion complexes specifically designed to catalyze peroxide bleaching (17). They function as powerful lignin oxidants that are regenerated *in situ* by hydrogen peroxide.

The effectiveness of hydrogen peroxide may also be enhanced by the addition of organic compounds that either participate in the reactions with lignin, for example by reacting with peroxide to form an intermediate with enhanced reactivity toward lignin, or by catalysis of lignin oxidation. One example is nitrilamine, which has been hypothesized to react with peroxide to form a peroxyimidic acid that in turn oxidizes lignin. Recently, however, evidence has been obtained for the existence of a free radical pathway (18). Another effective peroxide activator is tetraacetylenediamine (TAED). Table 2 (19) shows that it can be used to decrease both the peroxide charge and the required time to reach a given final brightness in the QPP sequence.

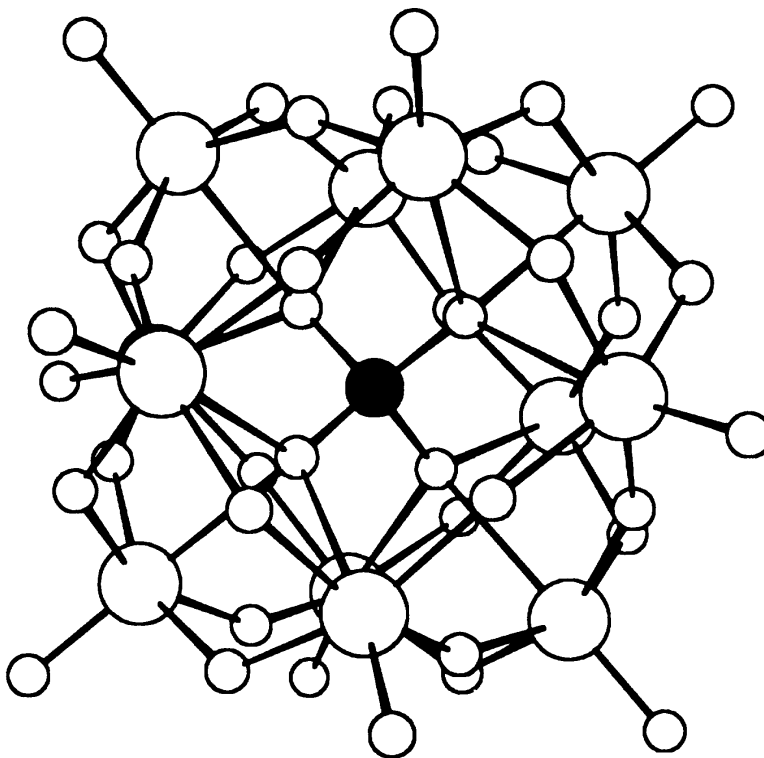
**Table 3. Effect of TAED in the P<sub>1</sub> stage of a QP<sub>1</sub>P<sub>2</sub> sequence applied to hardwood sulfite pulp (2% H<sub>2</sub>O<sub>2</sub> in P<sub>2</sub>).**

| H <sub>2</sub> O <sub>2</sub> , % | TAED, % | Time, min | Final Brightness |
|-----------------------------------|---------|-----------|------------------|
| 0                                 | 0       | 0         | 76.2             |
| 2                                 | 0       | 120       | 85.5             |
| 0.5                               | 0.5     | 60        | 85.2             |

The effectiveness of TAED is due to its ability to convert hydrogen peroxide to a compound that is itself capable of bleaching pulp, peracetic acid. Peracetic acid is one of a class of compounds, the peroxyacids or peracids, that have been proposed for use in pulp bleaching and are, in fact, used commercially. Both peracetic acid and peroxymonosulfuric acid (Caro's acid), as well as their mixtures, have been used. Peracids are capable of both delignifying pulp and brightening it.

Polyoxometalates (POM's), a class of polymeric metal oxide anions formed from simple oxides of vanadium, molybdenum or tungsten, have oxidized forms that are capable of oxidizing lignin and being regenerated by oxidation with oxygen or hydrogen peroxide. Figure 8 shows the chemical structure of a POM that is effective as a peroxide delignification catalyst. When added at a concentration of 2 mmol/L to a 4% consistency pulp suspension containing a charge of 2% H<sub>2</sub>O<sub>2</sub> based on pulp, the extent of delignification achieved was 48% higher than when no catalyst was used (20). Similar

results were obtained when the POM was added to oxygen and ozone systems. The selectivity was better for the latter two systems.



**Figure 8. Example of a polyoxometalate. Structure of a molybdovanadophosphate heteropolyanion,  $[PM_{12}O_{40}]^{3-}$ , in which M (large colorless ball) is either Mo or V, the central atom (dark ball) is phosphorus, and the small colorless balls represent oxygen atoms (20).**

The use of POM's as catalysts in peroxide, oxygen and ozone stages was inspired by the earlier discovery that POM's in their oxidized forms were effective as delignifying agents under anaerobic conditions (21). This led to a research and development program, still in progress, to develop a process based on the concept illustrated in Figure 9 (22). An aqueous solution of POM is applied to the pulp under anaerobic conditions. It oxidizes and degrades the lignin and itself becomes reduced in the process. The spent liquor containing the reduced POM and the dissolved organic material (mostly oxidized lignin) is separated from the pulp and oxidized with oxygen at high temperature. The reduced POM catalyzes the destruction of the organic material, converting it to carbon dioxide and water. At the same time, the oxidized form of the POM is regenerated and can be used again for bleaching.

From an environmental standpoint, this process is very attractive, since it emits only carbon dioxide and water and uses no chlorine compounds. It is also capable of high

degrees of delignification, for example, reducing the kappa number of southern pine pulp from 65 to 4 with acceptable viscosity and yield. It should be noted, however, that the process is not yet developed to the point of commercialization. Considerable engineering development is still needed to realize the extremely high POM recoveries needed to make it economically feasible.

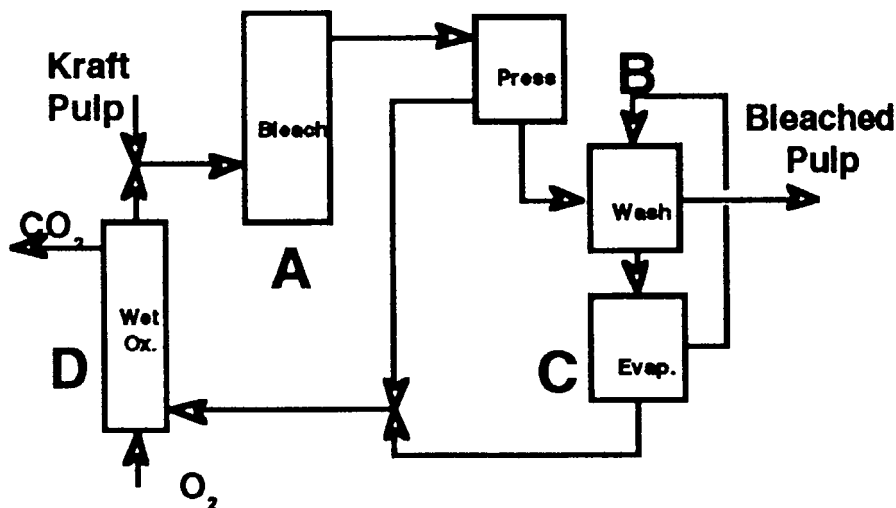


Figure 9. Polyoxometalate delignification process (22).

Another environmentally attractive process that is not yet at the stage of commercial feasibility is dioxirane delignification. Dioxiranes are formed when ketones are oxidized with Caro's acid. The most extensively investigated example is dimethyldioxirane (23), made by oxidizing acetone. Its structure is that of a three membered ring made up of two oxygen atoms and a carbon atom, with two methyl groups attached to the carbon atom. The strained ring structure makes it a very reactive oxidizing agent which is nevertheless selective, having little tendency to oxidize cellulose. Although its pulp bleaching efficacy was demonstrated in the early 1990's, it has not yet been used commercially. The chief reasons for this are associated with the complexity of the necessary on-site generation system. Such a system would incorporate subsystems for peroxide oxidation of sulfuric acid to Caro's acid, Caro's acid oxidation of acetone, and recovery of acetone.

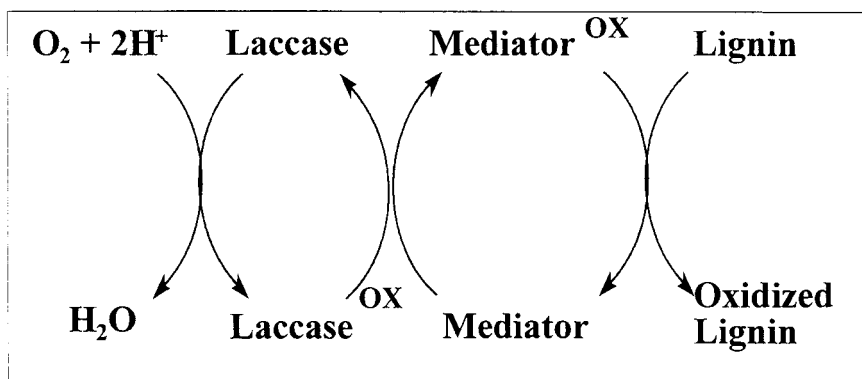
## Enzymes in Bleaching

Enzymes are biological catalysts known for their specificity and for their effectiveness when added in very small amounts. Two types have been shown to be effective in pulp bleaching applications: hemicellulases and redox enzymes.

Enzymes that degrade hemicelluloses can enhance lignin removal in subsequent bleaching stages (24). Xylanases have been studied the most and are generally the most effective, although mannanases have been shown to have some effect. Although the mechanism is not known with certainty, xylanase probably functions by removing xylan

from the fiber surface and within interstitial pores, providing freer access to the lignin by the bleaching agent and freer egress by the lignin fragments from the fiber. When applied prior to a chlorine dioxide delignification stage, chlorine dioxide savings on the order of 20% may be realized in that stage. Several mills currently use xylanases on a routine basis.

Unlike hemicellulases, redox enzymes directly result in lignin degradation and solubilization (25, 26). They are oxidizing agents capable of depolymerizing lignin and then being regenerated by contact with oxygen in the pulp suspension. Laccase is the one that has been most extensively investigated. Laccase by itself, however, is not capable of removing significant amounts of lignin from kraft pulp. It is believed that this is because the very large size of the laccase molecule prevents it from entering the fiber wall and accessing the lignin. This difficulty has been circumvented by adding a third component to the system, a compound known as a “mediator.” The mediator is a smaller analog of the enzyme that is capable of both being oxidized by the enzyme and oxidizing lignin. Thus, the enzyme is converted to its oxidized form by oxygen and, in turn, oxidizes the mediator. The oxidized form of the mediator can then diffuse into the fiber wall and oxidize lignin, being converted to its reduced form in the process. This then diffuses from the fiber and becomes re-oxidized by the enzyme, completing the cycle. Figure 10 (27) illustrates this process.



**Figure 9. Proposed laccase-mediator delignification mechanism (27).**

Redox enzymes are not in commercial use for pulp bleaching, principally because the cost of the mediator is too high. The most effective mediators discovered to date are 1-hydroxybenzotriazole and violuric acid. Both are nitrogen-containing heterocyclic compounds capable of forming radicals. It seems likely that economical mediators will eventually be found.

### Hydrolysis of Hexeneuronic Acids

The lignin content of unbleached kraft pulps, and therefore their bleach demand, is nearly always determined by measurement of kappa number, the amount of potassium permanganate consumed by a unit weight of pulp under controlled conditions. Up until a few years ago, it was tacitly assumed that only the lignin component of the pulp

consumed permanganate. This assumption was recently shown not to be universally applicable when it was discovered that the xylan present in wood, especially hardwoods, is partially converted during pulping to hexeneuronic acids (28). Furthermore, these hexeneuronic acids contain double bonds which make them reactive towards oxidizing agents, including both potassium permanganate and bleaching agents such as chlorine dioxide. The practical consequence of this is that chlorine dioxide is consumed not only by the lignin in the pulps to which it is applied, but also by any hexeneuronic acids that may be present. In hardwood kraft pulps, hexeneuronic acids may account for as much as 50% of the kappa number. It follows that prior removal of the hexeneuronic acids would result in a significant reduction in the amount of chlorine dioxide needed to bleach the pulp.

It turns out that there is a relatively simple means of removing the hexeneuronic acids prior to bleaching, because they are susceptible to removal by acid hydrolysis (29). Subjecting the pulp to a prehydrolysis stage can substantially reduce chlorine dioxide consumption. Such a prehydrolysis stage has been commercially implemented by at least one mill (30). Potential drawbacks are the relative slowness of the hydrolysis and the consequent large size of the vessel needed.

## **Summary and Conclusion**

Kraft pulp bleaching technology has undergone remarkable changes during the last decade, and the pace of change remains high. The growth of oxygen delignification intensified, mills learned how to use chlorine dioxide to replace all of the chlorine in the chlorination stage, and peroxide appeared in many more bleach plants than it had in the past. Ozone made its debut in 1992, and enzymes followed shortly thereafter. Compounds previously unknown by the industry suddenly became worthy of consideration as future bleaching agents -- dioxiranes, polyoxometalates, peracids. All of these technologies continue to evolve, becoming established, assuming new forms or getting closer to commercialization.

Two-stage oxygen systems have been developed for increased extents of delignification. This will allow pulp yields to be increased by terminating the kraft cook at a higher than normal kappa number and using the more selective oxygen system to complete the delignification.

The strong movement away from bleaching with molecular chlorine has resulted in rapid adoption of ECF bleaching, which is already used for more than half of the worlds bleached chemical pulp production. A recent development is the introduction of "Rapid D<sub>0</sub>" bleaching, in which the chlorine dioxide stage is conducted with a retention time so short (60-120 seconds) that the bleaching tower normally required for this stage can be completely dispensed with. This is a low capital cost alternative to the installation of a conventional, long retention time stage. Its availability also increases the number of options available to mills that must reconfigure their chlorine-based bleach lines to comply with the new AOX regulations.

It has been shown that the effects of digester conditions on pulp bleachability can be substantial. At high brightness levels, the differences in brightening stage ClO<sub>2</sub>

requirements can be as high as 60%. This finding opens the door to developing practical means of achieving improved bleachability through adjustment of pulping conditions.

The use of ozone to delignify kraft pulp was first commercialized in 1992 and has since been rapidly adopted by other mills. In October, 1998, there were reported to be a total of 20 ozone bleaching stages in commercial operation. Among recent developments in the area of ozone bleaching technology is the use of ozone and chlorine dioxide in the same bleaching stage. This approach allows the amount of chlorine dioxide in the delignification stage to be reduced, which has the beneficial effect of reducing AOX generation and may allow some mills to reach their effluent quality targets without installing new chlorine dioxide generation capacity.

Alkaline hydrogen peroxide, long known as an effective brightening agent in chemical pulp bleaching sequences, has found application as a delignifying agent. The viability of peroxide as a delignifying agent became established when technology was developed for efficiently controlling the detrimental effects of trace metals by chelation. This allows the conditions in the following peroxide stage to be made more severe, forcing the peroxide to bleach the pulp without extensive losses due to peroxide decomposition. Its effectiveness may be further enhanced by pressurization with oxygen. The resulting "pressurized peroxide" or (PO) stage has been extensively commercialized.

Future applications may employ metal ion complexes specifically designed to catalyze peroxide bleaching. Research has shown that they can function as powerful lignin oxidants that are regenerated *in situ* by hydrogen peroxide. The effectiveness of hydrogen peroxide may also be enhanced by the addition of organic compounds that either participate in the reactions with lignin, for example by reacting with peroxide to form an intermediate with enhanced reactivity toward lignin, or by catalysis of lignin oxidation.

Polyoxometalates (POM's), a class of polymeric metal oxide anions formed from simple oxides of vanadium, molybdenum or tungsten, have oxidized forms that are capable of oxidizing lignin and being regenerated by oxidation with oxygen or hydrogen peroxide. This may lead to the development of an environmentally attractive process employing POM's to delignify pulp and providing for recovery, regeneration, and re-use of the POM's with simultaneous destruction of organic byproducts. Similarly, dioxiranes may become the basis of another environmentally attractive pulp bleaching process.

Biotechnology also shows considerable promise for improving the bleaching process. Two types of enzymes have been shown to be effective in pulp bleaching applications: hemicellulases and redox enzymes. Application of a particular class of hemicellulases, xylanases, to pulp prior to a chlorine dioxide delignification stage can result in chlorine dioxide savings on the order of 20% in that stage. Several mills currently use xylanases on a routine basis. Unlike hemicellulases, redox enzymes directly result in lignin degradation and solubilization. Laccase is the most relevant example. Although it is ineffective alone, it has been found that addition of laccase together with another compound, called a mediator, results in extensive delignification.

Finally, the recent discovery of hexeneuronic acids in kraft pulps has implications that will affect the future course of bleaching development. Hexeneuronic acids contain double bonds which make them reactive towards bleaching agents such as chlorine

dioxide. Subjecting the pulp to a prehydrolysis stage can substantially reduce chlorine dioxide consumption.

All of these technologies may be expected to evolve further, some through continued research and some through both research and the accumulation of operating experience. It also seems certain that they will be joined by new ones, as research responds to unrelenting pressures for improved environmental performance of bleached chemical pulp production facilities.

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