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Advances in the Science and Technology of Chlorine Dioxide Delignification

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Advances in the Science and Technology of Chlorine Dioxide Delignification

**International Symposium Celebrating the 10th Anniversary
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ABSTRACT

Chlorine dioxide is rapidly replacing chlorine as the bleaching agent of choice for use in the first stage of bleaching sequences for kraft pulps. This paper reviews several investigations of the chlorine dioxide delignification process and some of its fundamental aspects. AOX, a surrogate for the environmental concerns that have driven the shift to ClO₂, can be predicted with the aid of an empirical model. The predictions indicate that improvements in ClO₂ delignification efficiency will be needed for environmental compliance in some cases and are desirable in any case. Rapid D₀ bleaching delignifies effectively and is beneficial in reducing the amount and improving the character of AOX formed in the D₀ and (EO) stages of the bleaching sequence. Studies of the relationships between ClO₂ bleachability

and residual lignin structure have shown that bleachability correlates positively with some lignin structural features and negatively with others. Vapor phase delignification of hardwood kraft pulps generates less byproduct chlorate and is remarkably more efficient than conventional, low consistency bleaching. It does, however, produce more AOX than conventional ClO₂ bleaching.

INTRODUCTION

After seven decades of reliance on chlorine as the primary bleaching agent for kraft pulps, the pulp and paper industry is on the verge of completing its abandonment of chlorine in favor of alternative oxidizing agents. Among the available alternatives, chlorine dioxide is emerging as the delignifying chemical of choice. This is partly due to its ability to extensively and selectively solubilize the residual lignin in kraft pulps, combined with its reasonable cost, well-developed technology for generation, storage, and handling, and the fact that it does not form significant amounts of chlorinated organic compounds as waste products.

Adsorbable Organic Halide (AOX)

The principal cause of the demise of chlorine has been its propensity to produce substantial quantities of a large variety of chlorinated organic byproducts. The amounts of such byproducts are collectively measured as the chloride ion they produce upon combustion, expressed

as “adsorbable organic halide,” or AOX. The amounts of AOX produced and released can be predicted from the results of laboratory studies and field data, as summarized in a recently developed statistical model.^{1,2} This model is strictly valid only for the bleaching of softwood kraft pulps. It predicts that the amount of AOX found in the combined filtrates of the first stage of the bleaching sequence and the subsequent caustic extraction stage will depend mainly on the amounts of chlorine dioxide and chlorine applied to the pulp in the first stage. More specifically, it predicts that between 11 and 13% of the Cl atoms applied in the first stage will be found in the combined filtrates from the first two stages.

The amount of AOX generated in the first two stages is only one of the factors that determines how much AOX will be released to the environment by a bleached kraft pulp mill. Additional AOX is generated in downstream brightening stages, for example in the D₁ and D₂ stages of a D₀(EOP)D₁ED₂ sequence. Other factors are the amount of AOX destroyed by alkaline hydrolysis reactions after the acid and alkaline filtrates mix in the mill’s sewer system and the amount that is destroyed by chemical and biological processes in the secondary effluent treatment system. The brightening stages are less efficient in converting Cl atoms to AOX, only about 2% of the Cl atoms added to those stages being converted. The model predicts 30-45% destruction on mixing and 40-50% destruction in the treatment system. The combined result, as predicted by the model, is that only 25-40% of the AOX generated is released to

the environment. In other terms, the model predicts that the amount of AOX released will be equivalent to the sum of 3-5% of the Cl atoms applied in the first stage and less than 1% of the Cl atoms applied in the brightening stages.

These percentages can be used as useful rules of thumb in predicting whether a given bleaching technology will meet a given regulatory limit on AOX release. As an example, one may wish to roughly assess the likelihood that using the D₀(EOP)D₁ED₂ sequence will enable a softwood kraft mill to comply with the United States Environmental Protection Agency’s monthly average AOX limit of 0.623 kg/tonne. As an example, consider that pulp is produced with an unbleached kappa number of 30, 2.5% ClO₂ (13 kg Cl/tonne) is applied in the first stage, and a total of 1.5% ClO₂ (8 kg Cl/tonne) is applied in the D₁ and D₂ stages. Under these conditions, the expected amount of AOX release is $(.04)(13) + (.01)(8) = 0.6$ kg/tonne. The apparent conclusion is that regulatory compliance would be achieved, but this conclusion should be regarded as very tentative, since it takes no account of the degree of statistical uncertainty inherent in the model on which it is based. It is likely that an analysis of the degree of uncertainty involved would lead to the conclusion that approximately 25% of mills adopting the assumed technology would fail to achieve compliance.

RAPID D₀ BLEACHING

Our studies of how effluent quality depends on the conditions of ClO₂ delignification have included an

investigation of the effects of changing the duration of the ClO_2 stage.³ The results showed that restricting the duration of the ClO_2 delignification (D_0) stage to very short times sharply decreased the amount of AOX formed in the first two stages, while sacrificing relatively little delignification. These effects are illustrated in Figures 1 and 2.

Figure 1 shows that, as the reaction time is decreased from 30 minutes to 3 seconds, AOX formation in the D_0 stage is sharply reduced. A 30-minute D_0 stage generated 0.34 kg/t, while only 0.07 kg/t was produced in 3 seconds. The reduction is so great that, even though the AOX released from the (EO) stage does not change very much, the total amount of AOX formed in the first two stages is significantly reduced.

As might be expected, the amount of delignification achieved at very short retention times is somewhat less than in a conventional 30-minute stage, but the loss of delignification is small in relation to the decrease in AOX formation. Comparison of the (EO) kappa numbers in Figure 2 with the unbleached kappa number of 14.1 shows that, in these experiments, the one-minute D_0 stage achieved 84% of the delignification obtained in a 30-minute stage, while generating only 42% of the AOX.

An additional benefit of using very short D_0 retention times becomes apparent when the nature of the AOX produced is examined more closely. It is well known

that the chlorine atoms comprising the AOX from pulp bleaching represent an enormous variety of chlorinated organic compounds, most of which are present in extremely small amounts. The complexity of the mixture, and the fact that many of the compounds are polymeric and characterized, makes its detailed chemical analysis virtually impossible. As a practical alternative, we developed a fractionation protocol that separates the components of the mixture into classes of similar compounds.^{3,4}

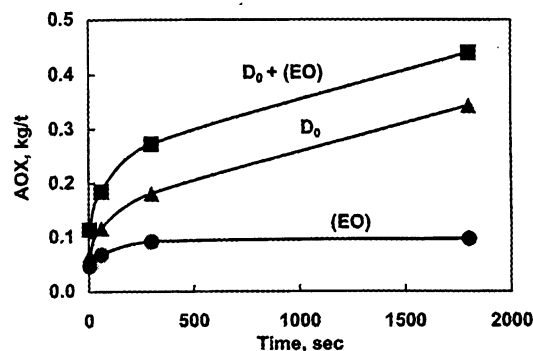


Figure 1. Effects of reaction time on AOX in D_0 and (EO) filtrates after bleaching 14.1 kappa oxygen delignified softwood kraft pulp at 0.25 kappa factor and quenching with excess Na_2SO_3 .

According to this protocol, the effluent was continuously extracted with ether for 96 hours, and the resulting extract was further fractionated into acids, phenolics and neutrals by successive extractions with aqueous NaHCO_3 and aqueous NaOH . The aqueous phase from the original ether extraction was then exhaustively extracted to give “polar” and “hydrophilic” fractions.

Volatile compounds were collectively determined by evaporating a separate sample of whole effluent and analyzing it before and after evaporation.

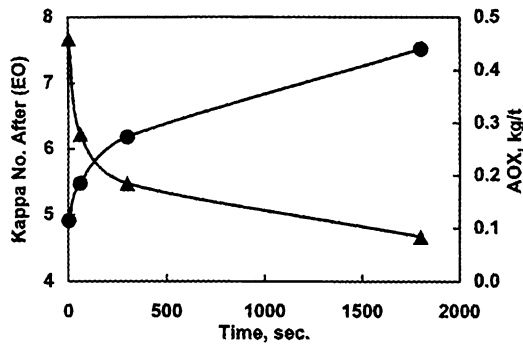


Figure 2. Effects of reaction time on kappa number after (EO) stage and sum of D_0 and (EO) filtrate AOX. Conditions as in Figure 1.

One result of such a fractionation procedure is information on the amounts of various types of material formed during bleaching, not just the total amount. This information is useful because it is known that some types are potentially harmful to the environment, while this is unlikely for other types. For example, the “hydrophilic” fraction, which is very soluble in water and completely insoluble in ether, is less likely to be harmful than the phenolic fraction, which is readily ether-soluble. Ether-soluble materials are likely to be retained in the fatty tissues of living organisms, where they can accumulate and possibly reach harmful levels. Also, they are more likely to be of lower molecular weight, and thus capable of entry into the cells of living organisms.

We also characterized the individual fractions in terms of their likely environmental significance. All fractions were analyzed for AOX and total organic carbon. The ratio of the two results, in molar terms, is the average number of chlorine atoms per carbon atom in the compounds contained in the fraction analyzed. The significance of this is that the probability of an organic chlorine compound being toxic is higher for compounds having greater chlorine contents (higher Cl:C ratios).

Figure 3 summarizes the results of both the fractionation and characterization of the individual fractions as a function of D_0 stage retention time. The areas of the circles are proportional to the total amounts of AOX produced at each of the retention times and the areas of the segments represent the amounts of the corresponding fractions. The darkness of the grayscale within each segment indicates the Cl:C ratio, as indicated by the scale at the bottom of the figure. It is apparent that, in addition to reducing the total amount of AOX, decreasing the D_0 retention time also decreases the proportion of the AOX that resides in potentially problematic fractions and decreases the likelihood that those fractions will be toxic. These latter benefits are of no consequence in relation to regulations written in terms of total AOX, but they may be significant in relation to current or future regulations governing chronic toxicity or more subtle effects on the environment.

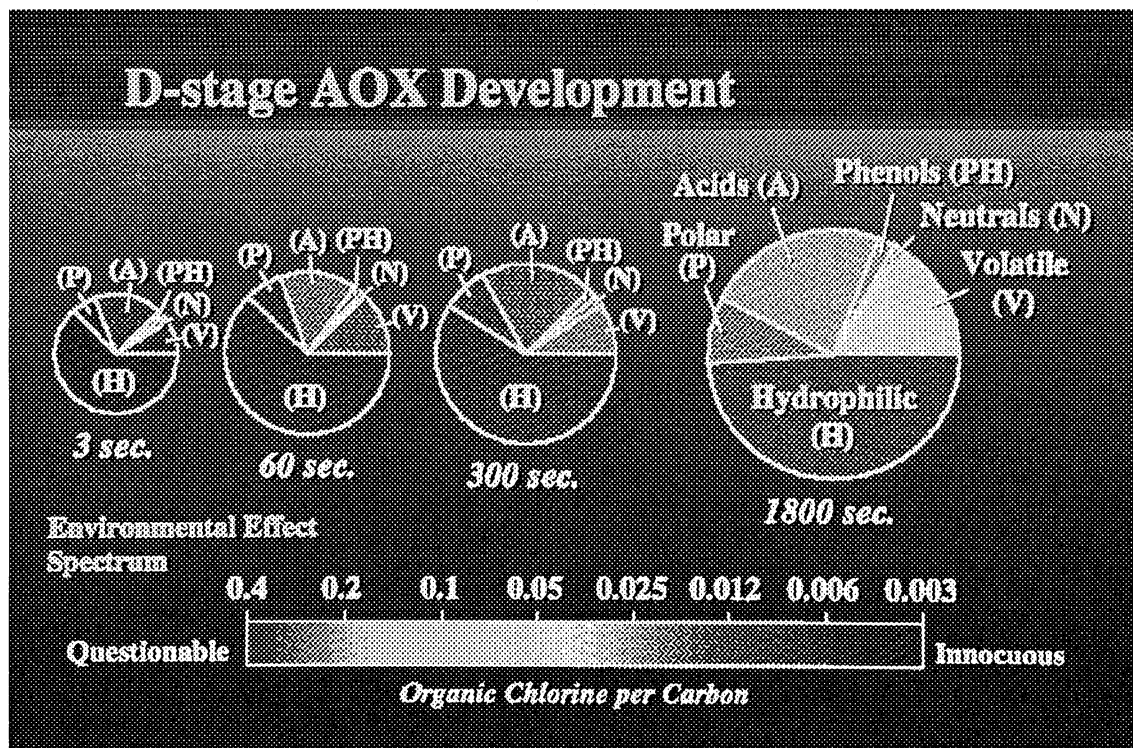


Figure 3. Effects of reaction time on amounts of AOX fractions formed in the D₀ stage (as indicated by segment areas) .

PROBING THE CHEMISTRY OF THE D₀ STAGE

Most studies of the reactions between ClO₂ and the residual lignin in kraft pulp have relied extensively on the use of model compounds as surrogates for lignin.^{5,6,7} More recently, however, nuclear magnetic resonance (NMR), coupled with lignin isolation and derivatization techniques, has enabled direct observation of the changes within the structure of the residual lignin itself.^{8,9,10} Figure 4, for example, shows ³¹P-NMR spectra of residual lignins isolated from two kraft pulps and then derivatized

with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.⁹ By integrating the signals over ranges associated with particular environments of the nucleus under examination, quantitative measures of the occurrence of particular structural features (functional groups and linkage types) can be obtained. In the case of the spectra shown in Figure 4, the signal associated with the ³¹P nucleus provides information on the type of hydroxyl group or quinonoid unit to which it has become attached in the derivatization process. In this way, it is possible to determine the amounts of guaiacyl (uncondensed)

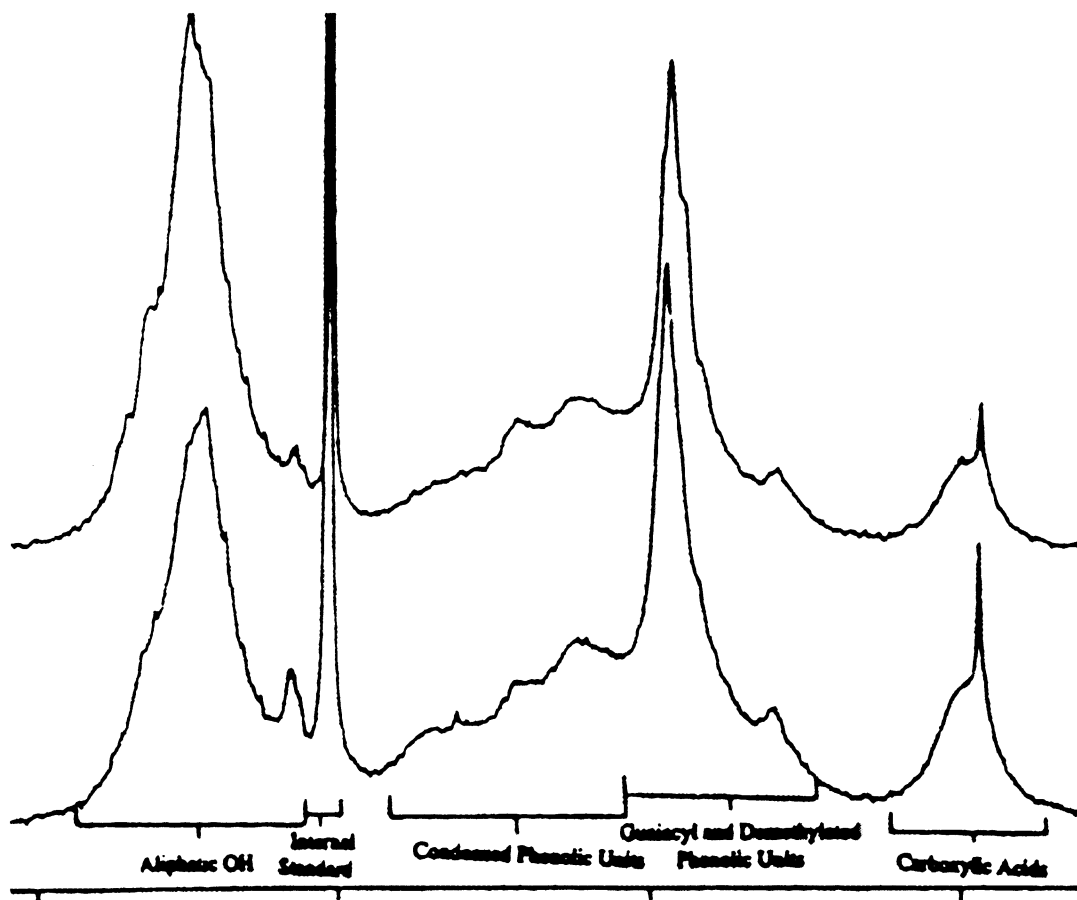


Figure 4. ^{31}P NMR spectra of derivatized EMCC[®] pulp residual lignins from pulps having unbleached kappa no. of 29 (upper curve) and 14.

phenolic units, condensed phenolic units, aliphatic hydroxyl groups, and carboxylic acid groups. Similarly, ^{13}C and ^1H NMR can be used with underivatized lignin samples. In the former case valuable information is obtained on the degree of substitution of the aromatic ring, the degree of condensation, or occurrence of difficult-to-break carbon-carbon linkages between aromatic units, and the

occurrence of more easily cleaved ether linkages, such as β -aryl ether linkages, between aromatic units.

Studies of the relationships between ClO_2 bleachability and residual lignin structure inferred from NMR spectra have begun to provide insight into mechanisms of the reactions involved. In a study conducted in our laboratories, Froass⁹ isolated lignin from pulps prepared from

southern pine (*Pinus taeda*) in simulations of both conventional and EMCC[®] kraft pulping at several kappa number levels in the range 14-29. The same pulps were also bleached by subjecting them to a D₀(EO) sequence. Measurements of the amount of lignin removed (as kappa number reduction, $\Delta\kappa$) and ClO₂ consumption (as equivalent chlorine or "total active chlorine," TAC) allowed the bleachability to be expressed as $\Delta\kappa$ /TAC. This bleachability measure was then correlated with the occurrence of various structural features in the residual lignins isolated

from the unbleached pulps, as determined by ³¹P and ¹³C NMR. The results are shown in Figure 5.

Bleachability correlated positively with the content of interunit ether linkages in the residual lignin; negatively with carboxyl group content; negatively with degree of condensation (as measured by the number of substituted carbons in each aromatic ring and the content of condensed phenolic units); and negatively with the content of uncondensed phenolic units. These observations show that

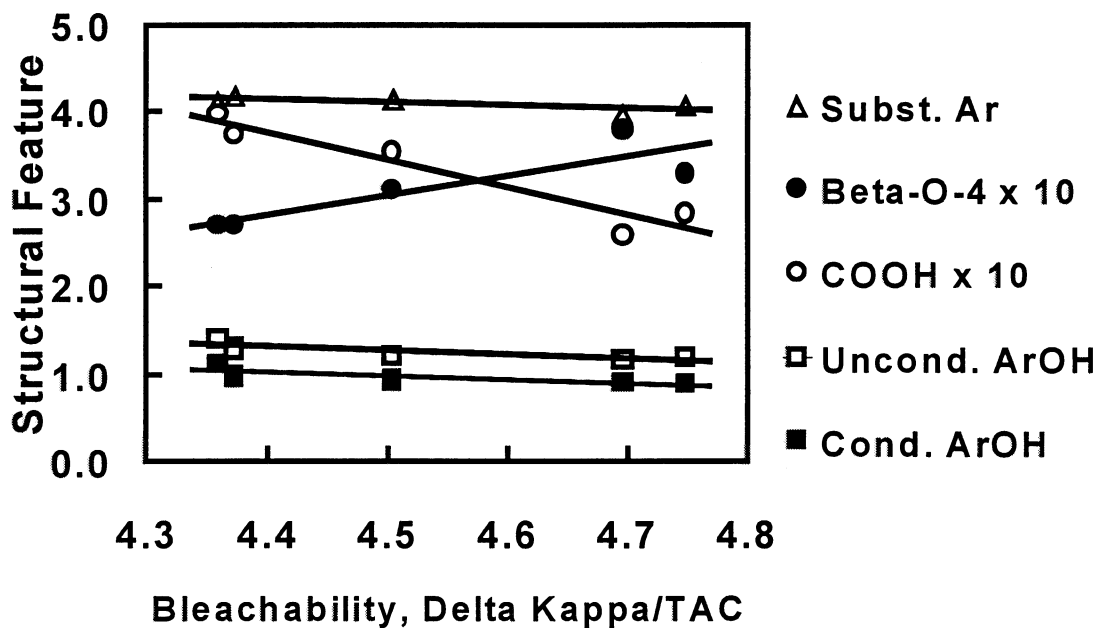


Figure 5. Correlations between bleachability and residual lignin structure, as determined by ¹³C (substituted aromatic C and aliphatic C in β -O-4 linkages) and ³¹P NMR. Units: no. of C atoms per aromatic unit (substituted aromatic C and aliphatic C in β -O-4 linkages) and mmol/g.

predictions based solely on the results of model compound experiments can be misleading. In particular, free phenolic hydroxyl units are considered to be particularly vulnerable to oxidation by ClO_2 on the basis of model compound behavior, yet lignins with higher levels of these groups were not more easily bleachable. This suggests that such groups, though readily attacked, do not contribute significantly to the integrity of the lignin macromolecule. This is consistent with the existing supposition that they represent "end groups," having only a single bond to the rest of the macromolecule. The negative correlation with degree of condensation suggests that this is a controlling factor. The negative correlation with carboxyl groups is somewhat surprising, in that lignin with more solubilizing groups might be expected to require less oxidative depolymerization (bleaching) for removal. Apparently, carboxyl groups have some other effect that is more important than their solubilizing effect, or the circumstances that lead to an increase in carboxyl content simultaneously cause other effects detrimental to bleachability.

VAPOR-PHASE BLEACHING

Although chlorine dioxide is normally applied to pulp as a dilute solution at low consistency, it may also be applied in the form of a gas, as a mixture with other gases such as air or water vapor. This mode of ClO_2 application has been proposed as a

means of achieving efficient delignification while simultaneously generating relatively small amounts of byproduct adsorbable organic halide (AOX).^{11,12} We have become interested in this process as a result of our studies of the interdependence of ClO_2 delignification efficiency, bleaching conditions, residual lignin structural changes, and byproduct generation. Accordingly, we have conducted vapor phase ClO_2 delignification experiments in the laboratory and have followed them with determinations of residual lignin structural changes and effluent AOX.¹³ We emphasized hardwood pulps made from sweetgum by laboratory simulations of both conventional and RDH kraft pulping. Some experiments were also conducted on pulps made from southern pine by laboratory simulations of conventional kraft pulping.

Vapor phase D_0 stage bleaching was done by passing a stream of nitrogen and chlorine dioxide through a rotating spherical flask containing fluffed pulp at 30% consistency maintained at 60°C.

As shown in Table I, vapor phase delignification of the hardwood pulps was remarkably more efficient than conventional, low consistency bleaching. In spite of the fact that less ClO_2 was consumed in the vapor phase experiments, the kappa number after extraction was 50% lower. Delignification efficiency in the $D_0(\text{EO})$ partial sequence, expressed as kappa number reduction per percent of active chlorine consumed, was 4.4-5.3 for the

vapor phase D₀ stage, as compared with 3.0-3.9 for the low consistency D₀ stage.

Information on the mechanisms of delignification and potential environmental effects was obtained by collecting and analyzing filtrates from each of the bleaching stages. The resulting data are presented in Figures 6 and 7. The yields shown in these figures represent the percentages of the chlorine atoms in the ClO₂ charged that are converted to the indicated species.

Striking features of the data in Figure 6 are the markedly higher rate of AOX generation in the vapor phase process than in the conventional one and the decreased AOX yield when low kappa number pulps are bleached. Figure 7 shows that vapor phase bleaching generates much less chlorate

ion than conventional bleaching. This is consistent with the greater efficiency of the former, since chlorate is an inert, high oxidation state product. Its formation represents a waste of the oxidizing power of ClO₂.

Previous work^{14,15} has shown that lignin reduces ClO₂ to chlorous acid (or chlorite ion, depending on the pH) and hypochlorous acid in parallel reactions. Subsequently, hypochlorous acid reacts with chlorite ion to form chlorate ion, which does not react further. Hypochlorous acid also reacts with water to form molecular chlorine which, in turn, reacts with organic substrates to form chlorinated organic compounds. The formation of the latter compounds is reflected by the measurement of AOX in the bleaching filtrate. Thus, the higher

TABLE 1. Vapor Phase Bleaching of Hardwood Kraft Pulps

Experiment	Process	Unbl. Pulp		D ₀ Stage			(EO) Stage			
		Pulp Type	Kappa Number	Kappa Factor	Kappa Number	Delta Kappa/TAC	NaOH Charge, % o.d.p.	Final pH	Kappa Number	Delta Kappa/TAC
HCC1	Conventional	Conv.	11.4	0.200	6.2	2.3	2.5	12.4	4.2	3.2
HCC2			15.2	0.200	7.9	2.4	2.0	12.0	5.2	3.3
HCR1		RDH	7.8	0.200	5.6	1.4	1.7	11.9	3.1	3.0
HCR2			13.4	0.200	10.0	1.3	1.7	12.0	5.2	3.1
HCR3			22.9	0.200	13.9	2.0	1.7	11.6	5.2	3.9
HVC1		Vapor Phase	Conv.	11.4	0.181	4.2	3.5	1.7	11.8	2.3
HVC2	15.2			0.171	5.3	3.8	1.7	11.8	2.5	4.9
HVR1	RDH		7.8	0.155	3.3	3.7	1.7	11.9	1.5	5.2
HVR2			13.4	0.172	5.4	3.5	1.7	11.8	2.8	4.6
HVR3			22.9	0.167	8.2	3.8	1.7	10.6	2.6	5.3

Notes: 1. D₀ stage conditions: For conventional bleaching, Quantum Mixer, 30 min., 45°C, 3% consistency, final pH 2.5-3.0. For vapor phase bleaching, rotating spherical glass reactor, 7-10 min., 60°C, 30% consistency, final pH 2.5-3.0.

2. (EO) stage conditions: Pin mixer, 60 min., 70°C, 10% consistency, oxygen pressure initially 60 psig. and decreased by 10 psig. every 5 min.

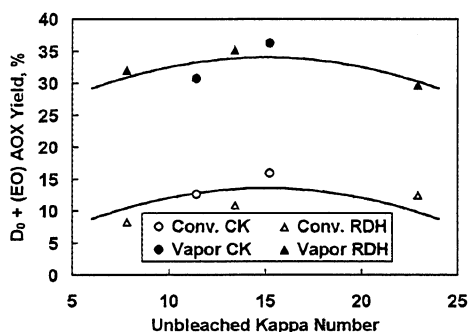


Figure 6. Sum of AOX yields from analyses of D_0 and (EO) stage filtrates

efficiency, higher rate of AOX generation and lower rate of chlorate ion formation all suggest that applying gaseous ClO_2 to high consistency pulp favors the initial formation of hypochlorous acid over that of chlorous acid or chlorite. The precise reason for this behavior is not yet apparent, but will be the subject of our continuing studies.

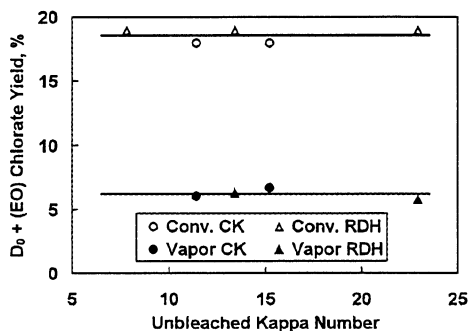


Figure 7. Sum of chlorate ion yields from analysis of D_0 and (EO) stage filtrates

SUMMARY AND CONCLUSIONS

Chlorine dioxide is rapidly replacing chlorine as the bleaching agent of choice for use in the first stage of bleaching sequences for kraft pulps. This is largely due to concerns about chlorinated organic byproducts and their embodiment in environmental regulations, such as the AOX limitations in the U.S. Cluster Rule. Empirical AOX models predict that, in many situations, complete substitution of ClO_2 for Cl_2 will be all that is required to reduce AOX discharges to satisfactory levels. In some cases, however, it is likely that additional measures will be needed. Improving the efficiency of ClO_2 delignification is one avenue toward more nearly universal environmental compliance. In any event, such improvements are desirable for economic reasons.

Rapid D_0 bleaching delignifies effectively and is beneficial in reducing the amount of AOX formed in the D_0 and (EO) stages of the bleaching sequence. In addition, it has a beneficial effect on the character of the AOX that is produced, reducing the size of fractions that may be considered harmful. This may be significant in relation to current or future regulations governing chronic toxicity or more subtle effects on the environment.

Studies of the relationships between ClO_2 bleachability and residual lignin structure inferred from NMR spectra have begun to provide insight into

mechanisms of the reactions involved. For example, in the bleaching of pine kraft pulps, it was found that bleachability correlated positively with the content of interunit ether linkages in the residual lignin; negatively with carboxyl group content; negatively with degree of interunit condensation; and negatively with the content of uncondensed phenolic units. These observations show that predictions based solely on the results of model compound experiments can be misleading.

Vapor phase delignification of hardwood kraft pulps was remarkably more efficient than conventional, low consistency bleaching. There was, however, a markedly higher rate of AOX generation in the vapor phase process than in the conventional one. Consistent with its greater efficiency, vapor phase bleaching also generates much less chlorate ion than conventional bleaching.

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