POLYOXOMETALATE BLEACHING OF KRAFT PULP: A HIGHLY SELECTIVE CLOSED MILL TECHNOLOGY.

I. A. Weinstock, R. H. Atalla, R. S. Reiner, M. A. Moen and K. E. Hammel
USDA Forest Service.
Forest Products Laboratory
Madison, Wisconsin U.S.A.

ABSTRACT

A process for using polyoxometalate (POM) salts and oxygen in the commercial bleaching of chemical pulps is herein described. A clear advantage of polyoxometalates over oxygen alone, hydrogen peroxide or ozone is their inherently high oxidative selectivity for the residual lignin in softwood kraft pulps. Softwood kraft pulps delignified to low kappa numbers using POM salts possess papermaking properties comparable to those obtained using chlorine/chlorine dioxide and alkali. The goal of ongoing research and development efforts is to develop a highly selective, oxygen-based polyoxometalate delignification and bleaching technology compatible with mill closure. To this end, several Unit Operations are under development. These include: Bleaching, pulp washing, wash water recovery, removal of salt impurities, wet oxidation of dissolved organic compounds, and aerobic oxidation of spent polyoxometalate salts to their bleaching active forms.

INTRODUCTION

Background

Since the start of POM bleaching research at the USDA Forest Service, Forest Products Laboratory, in January, 1992. Unit Operations necessary for commercial application of POM technology have been identified and the operation of critical Unit Operations has been demonstrated in the laboratory. The present contribution is the final paper in a recent series of introductory overviews concerning POM bleaching technology (14).

If its high oxidative capacity could be adequately channeled, oxygen, the least expensive alternative to chlorine or chlorine dioxide, would be an attractive choice. One way to control the reactivity of oxygen is by using transition-metal based reversible oxidants to mediate in the selective transfer of electrons from lignin to oxygen. This approach was suggested by the role transition metal ions play in the selective degradation of lignin by wood-rotting fungi. In this biological system, a chain of events catalyzed by metal-containing enzymes and complexes results in the net degradation of lignin by oxygen. POM complexes are uniquely capable of functioning in this capacity while, at the same time, satisfying the large set of criteria (low cost, low toxicity, water solubility, useful reaction rates, stability to process conditions, high recoverability, etc.) necessary for commercial application.

POM complexes are remarkably stable to oxidizing conditions and high temperatures and include a wide variety of water-soluble inorganic compounds, many of which are easily prepared from common, non-toxic mineral oxides. The term "polyoxometalates" refers to a class of discrete polymeric metal-oxide anions that form spontaneously when simple oxides of vanadium (+5), molybdenum(+6) or tungsten(+6) are combined under the appropriate conditions in water (5). In a great majority of polyoxometalates, the transition metals are in the d6 electronic configuration which dictates both a high resistance to oxidative degradation and an ability to oxidize other materials such as lignin. A variety of POM formulations and structural types are potentially useful in bleaching. To date, three complexes, all of the Keggin (5) structural class and possessing either vanadium(+5) or Manganese(+3), have been studied in the context of pulp bleaching.

The POM bleaching process now being developed will use a highly selective and completely regenerable POM bleaching agent. To achieve mill closure, a strategy that parallels the recovery principles used in kraft pulping is envisioned. In bleaching, fully oxidized POM complexes are reacted with unbleached pulp under anaerobic conditions. During oxidative bleaching, the POM complexes are reduced and oxidized residual lignin fragments are dissolved by the bleaching liquor. Afterwards, the reduced POM liquor is reoxidized by oxygen under conditions that convert dissolved lignin fragments to carbon dioxide and water. Thus, the POM liquor can be continually reused with mill closure achieved by use of a recovery system, in which, analogously to the kraft recovery system, active POM liquor is reactivated and organic materials consumed.

Closed Mill Polyoxometalate Bleaching Process

As currently envisioned, an effluent-free polyoxometalate bleaching mill will consist of four Unit Operations: A Anaerobic bleaching; B Pulp washing; C Concentration of wash water and removal of undesired inorganic salts; and D Aerobic polyoxometalate-catalyzed wet oxidation of dissolved organic materials with simultaneous regeneration of the polyoxometalate to its bleaching-active form (Figure 1).

In bleaching, (unit operation A, Fig. 1) the polyoxometalates are dramatically more selective than molecular oxygen and yet have the attractive property that after use in bleaching, the reduced polyoxometalates can be reoxidized with oxygen (unit operation D, Fig. 1). Bleaching and the regeneration of used bleaching liquors are each carried out in separate steps (6). In the bleaching step (represented in eq. 1) mixtures of water, pulp and a fully oxidized polyoxometalate (POMox) are heated anaerobically. During the reaction, the polyoxometalate is reduced (POMred) as residual lignin is oxidized. After the reaction, the spent bleaching liquor is separated from the pulp and reoxidized using oxygen as represented by eq. 2 (stoichiometry undefined).

\[
POM_{ox} + \text{pulp} \rightarrow \text{Bleached pulp} + POM_{red}
\]

(1)

\[
POM_{red} + O_2 + 4H^+ \rightarrow POM_{ox} + 2H_2O
\]

(2)

By separating aerobic reoxidation of POMred from anaerobic bleaching, oxygen can be utilized as a terminal oxidant while avoiding exposure of the pulp to non-specific oxygen radicals. Because the polyoxometalates (POMox and POMred) only serve in a mediating role for oxygen, carbon dioxide and water are the only by-products of the bleaching chemicals.

After leaving the bleeding reactor, the pulp is washed with a series of high pressure diffusion washers (unit operation B, Fig. 1). Theoretical arguments and preliminary washing studies show that the POMs are not adsorbed onto pulp fibers. Thus, unlike removal of caustic, removal of POM from the pulp is likely controlled by diffusion phenomena alone. Indeed, laboratory washing experiments currently in progress show that POMs can be quickly and easily removed from pulps with distilled water. In practice, one washing strategy might be to use a countercurrent scheme. Wash water would be recycled by evaporation, using heat provided by low grade steam. After concentration, a small spent liquor stream may be diverted so that inorganic salts carried in with the pulp can be removed using cation exchange or crystallization (unit operation C, Fig. 1). It is anticipated that some POM will be removed at this or a separate point and re-refined at a rate dictated by its operational half-life.

The spent liquor is then sent to unit operation D, the purpose of which is two-fold: to oxidatively degrade dissolved lignin fragments to volatile organic materials, carbon dioxide and water (wet oxidation) and to return the POM to its active form (eq. 2).
Although the POMs act with high selectivity in the anaerobic bleaching reaction with pulp, the conditions in the wet oxidation unit will be significantly more aggressive, including higher temperatures and the introduction of oxygen (Fig. 2). Under these conditions, the POMs act both as catalysts and initiators in the aerobic oxidation and autoxidation of dissolved organic materials. This is where the high thermal stability and resistance to oxidative degradation of the POMs are used to their fullest advantage. The POMs are stable under conditions wherein even very robust synthetic metallocorphyrins are susceptible to oxidative degradation (7). Upon cessation of the wet oxidation reactions, the liquor, now containing active POM$_{ox}$, is returned to the bleaching reactor.

What follows is a presentation of results obtained in laboratory demonstrations of unit operations A and D and an assessment of the studies and developments needed prior to pilot-scale trials.

**EXPERIMENTAL**

**General Methods**

Two unbleached mixed-pine kraft pulps, one with a kappa number of 33.6 and a viscosity of 34.2 mPa·s, and one with a kappa number of 24.1 and a viscosity of 27.8 mPa·s were used. Microkappa numbers were obtained using Technical Association of the Pulp and Paper Industry (TAPPI) useful method um-246 and handsheets were prepared using TAPPI test method T218 om-83. The full range of papermaking properties were determined using appropriate TAPPI test methods. Bleaching studies were performed using a vanadotungstosilicate salt, K$_5$SiVW$_{11}$O$_{40}$ (POM$_{ox}$, form), which was prepared by ozone treatment of a solution of K$_5$SiVW$_{11}$O$_{40}$ (POM$_{red}$ form) (8) to which had been added a vanadomolybdophosphate acid-salt, K$_6$SiMo$_{10}$V$_2$O$_{40}$ (POM$_{red}$ form) (9) to which there had been added a stoichiometric amount of sulfuric acid. Wet oxidation studies were performed using an equilibrium mixture of vanadomolybdophosphate acid-salts, Na$_2$H$_2$[PMO$_{10}$O$_{40}$]$_2$ (2) and Na$_2$H$_2$[PM$_2$V$_8$O$_{40}$] (10) in which 2 is favored and where the ratios x/(4-x), x/(5-x) and x/(6-x) are determined by pH (9). Where more than one vanadium ion is present in the polyanion, positional isomers are observed by $^3$P NMR of aqueous solutions. For convenience, this mixture of vanadomolybdophosphate salts is identified by the salt in greatest abundance, 2, often referred to as PV$_2$Mo$_{10}$E. Standard methods were used to quantify the degradation of dissolved organic compounds that occurred during wet oxidation. The first method involved measuring the chemical oxygen demand (COD) of the solutions and the second entailed measuring the amount of carbon dioxide evolved (10.11). $^3$P NMR spectroscopy was used to confirm that degradation oft did not occur during wet oxidation. K$_5$SiVW$_{11}$O$_{40}$ (1) was chosen for demonstration of POM bleaching because it is stable at neutral pH, at which cellulose hydrolysis occurs relatively slowly at elevated temperatures. At neutral pH in water, a 0.05 M solution of 1 has a half-life of over 20 years at 100°C. The disadvantages of using 1 commercially are that it reacts slowly with phosphate (the most obvious nonvolatile inorganic buffer available for maintaining a pH of 7) and reacts too slowly with oxygen to meet the needs of commercial bleached pulp production rates. PV$_2$Mo$_{10}$E is extraordinarily stable at pH values of 0 to 4, and reacts rapidly with oxygen. It is used here to demonstrate wet oxidation (unit operation D) but is unsuitable for use at the pH values envisioned for commercial application. A single POM formulation with the requisite properties for effective operation in both operations A and D is being developed.

**Bleaching**

POM treatment of unbleached kraft brownstock was divided into three successive batch oxidations, V$_1$, V$_2$, and V$_3$. In the first set of bleaching trials, a pulp with a kappa number of 33.6 and a viscosity of 34.2 mPa·s was used. A mild anaerobic alkali extraction was performed prior to the POM bleaching. This treatment had little effect and was dropped in later work. V$_1$ stages were run in a stirred, glass-lined, high pressure Parr reaction vessel. The pulps were slurried at 3% csc in a pH 7 phosphate buffer and purged with nitrogen. The reactor was then heated to 125°C (ramp time of 40 min.) and held at temperature one hour for V$_1$, and 1.5 hrs for V$_2$ and V$_3$. The reactor pressure was sustained with nitrogen at about 340 kPa. During bleaching, the pH slowly decreased from seven to no lower than six. The liquor changed from a bright yellow color of fully oxidized 1 to the dark purple of the reduced material. After each batch reaction the pulps were collected in a Buchner funnel and washed three times with water. A parallel control sequence was performed by heating mixtures of pulp, water and inorganic buffer in three successive batch reactions but with no polyoxometalate present. Both sequences were followed by anaerobic extraction with 1% NaOH for two hours at 85°C with pulp consistencies (csc) of 1-2%. In addition, two samples of the unbleached pulp were each partially delignified using chlorine and alkali (CE). In one case, 7.4% chlorine was applied to unbleached pulp, and in the second case, 9.0% chlorine was applied to a different sample of unbleached pulp.

For determination of papermaking properties, a POM delignified pulp was compared to a pulp delignified using a (C/DE)E sequence. Due to an insufficient supply of the original unbleached pulp, a new supply, in this case having an initial kappa number of 24.1 and a viscosity of 27.8, was used. This pulp was delignified in triplicate by oxidation reaction. The amount of carbon dioxide produced and the COD of the organic compounds in the liquor were measured. The pH of three was maintained by periodic addition of small amounts of a dilute sulfuric acid. Bleaching was carried out in a stirred high pressure Parr reaction vessel with a glass liner at 100°C for 4 hours under nitrogen. The dark green reduced liquor was then pressed from the pulp and treated with oxygen (wet oxidation) to degrade the dissolved organic compounds removed from the pulp during bleaching. The reaction was done in a glass-lined Parr reactor equipped with a gas entrainment impeller designed to circulate head gasses through the solution. The reaction was carried out at 150°C for 4 hours under an oxygen partial pressure of 800 kPa. The red, fully-oxidized liquor was then used for bleaching in the next bleaching/wet oxidation cycle. After every bleaching and wet oxidation reaction, the amount of carbon dioxide produced and the COD of the organic compounds in the liquor were measured. The concentration of 2 was followed titrametrically and its integrity was verified by $^3$P NMR spectroscopy. The extent of delignification associated with each bleaching reaction was determined by kappa number.
RESULTS AND DISCUSSION

Bleaching

Microkappa numbers and viscosity values for the average of three EV,V,V,E bleaching sequences, a control sequence and two different CE bleaching reactions, obtained using two CI loadings are shown in Figure 3A (12). The unbleached pulp had an initial kappa number of 33.6 and a viscosity of 34.2 mPa·s. The two CE runs are presented together as a single curve. The POM bleaching sequence is as selective as the CE sequence down to a kappa number of 10 (7.4% Cl) and more selective at lower kappa numbers (9.0% Cl). It is noteworthy that the viscosity of the pulp subjected to the control run (no POM present) dropped almost in parallel with that of the POM trials. This suggests that the reaction conditions cause some cellulose hydrolysis and that the oxidative selectivity of the POM bleaching agent might be substantially higher than that of chlorine and alkali. To the extent that optimization of reaction conditions: time, temperature, POM concentration, etc., can minimize the degree of cellulose hydrolysis, the selectivity of the overall process is expected to improve (see below).

A V,V,V,E sequence was performed on a larger scale to provide pulp for the determination of papermaking properties (see experimental). As shown in Figure 3B, the kappa-viscosity curves of the POM trials fall slightly below those obtained using the (C/D)/E sequence. Average yield of the POM delignified pulps was 89 ± 3%, while that of the POM-free control was 89% and that of the (C/D)/E treated pulp was 95%. Significantly, the yield of the POM-free control reaction is identical to the average yield of the unoptimized POM trials. Further evidence that cellulose hydrolysis is responsible for the drops in viscosity observed in each cases. (In this regard, it should also be noted that the pH values of the POM liquors dropped to near six during bleaching, while that of the control reaction remained at seven throughout.) Even so, the POM delignified pulps possess papermaking properties close to those of the C/D delignified sample (Table I). The C/D delignified pulps possess slightly higher tensile index, breaking length and zero-span index values, while the POM pulps possess higher tear index, TEA index and elongation % values. These observations lead us to believe that, with optimization of reaction conditions, the papermaking properties of POM delignified pulps could easily match or exceed those of pulps delignified with elemental chlorine and chlorine dioxide. For example, by using a 10-fold higher concentration of POM and running the bleaching reaction for 30 min at 125 °C, the pulp used for the experiments described in Figure 3B was delignified to a microkappa no. of 4.7 and a viscosity of 23.0 mPa·s after alkali extraction. (Only 15% of the POM was consumed.) Finally, the POM reactions described here were run at pH 7 (phosphate buffer). POM complexes designed to operate at pH 9 are currently being formulated. At pH 9, less cellulose hydrolysis is expected to occur, while, at the same time, the POM complexes will likely react more rapidly with phenolic end groups present in residual lignin (13). Both trends are expected to facilitate further optimization of the POM delignification reactions and allow for selective delignification down to very low kappa numbers.

Mechanism of POM Delignification

Recent model studies using 1 and both phenolic and non-phenolic lignin models suggest that, under bleaching conditions, only phenolic compounds are degraded at a useful rate. This result should be evaluated in light of the generally accepted views that oxygen delignification proceeds via a net reaction of O₂ with phenolate anions and that selectivity decreases dramatically once these structures are consumed. Unlike the direct application of oxygen, POM treatments are highly selective. If the POMs initiate lignin degradation reactions by reacting only with phenols, a rapid drop in the phenolic content of POM treated residual lignin should result in a sharp drop in the rate of delignification. However, no such drop in bleaching activity is observed during POM delignification to low kappa numbers. One possibility is that phenolic moieties are continually introduced as new end-groups in the lignin polymer as POM delignification proceeds.

POM Treatment of Oxygen Delignified Pulps

If POMs react primarily with phenolic end-groups, how effectively will POMs bleach oxygen delignified kraft pulps? In preliminary experiments, we have found that oxygen delignified kraft pulps are delignified to low kappa numbers under the same condition as those used for the delignification of untreated brownstock. This raises interesting questions regarding the chemical composition and macromolecular structure of O₂ delignified pulps, and the mechanism(s) of POM delignification.

A related question is whether POM complexes can be used for selective brightening. Preliminary studies suggest that this can be achieved. Here also, the reactivity of residual lignin fragments remaining in substantially delignified pulps (i.e., below a kappa number of approximately 4) must be considered side-by-side with a discussion of their accessibility.

Wet Oxidation

During bleaching, lignin and its fragments enter the POM bleaching liquor. To achieve mill closure, it is necessary to remove them. In unit operation D, the POM complexes can be used to catalyze and initiate the aerobic degradation (wet oxidation) of the dissolved organic compounds to carbon dioxide and water (14). POM complex 2 was used to demonstrate the feasibility of wet oxidation because its reduced form reacts rapidly with oxygen (9). Initial studies using 2 in solution with model compounds suggested that addition of a sacrificial reductant might be necessary to maintain a concentration of energetic oxygen-centered radicals high enough to degrade recalcitrant, partially oxidized organic species as the reaction

Table 1. Selected papermaking properties of POM delignified and C/D delignified kraft pulps.

<table>
<thead>
<tr>
<th>Property</th>
<th>POM Delignified</th>
<th>C/D Delignified</th>
</tr>
</thead>
<tbody>
<tr>
<td>YIELD (%)</td>
<td>89 ± 3%</td>
<td>95%</td>
</tr>
<tr>
<td>TEA INDEX (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ELONGATION (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZERO-SPAN (%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Figure 3](image3.png)

![Figure 4](image4.png)
neared completion. It was then recognized that the bleaching reaction itself might serve as a source of sacrificial reductants in the form of the lignin and related fragments dissolved during selective anaerobic bleaching. In the spent liquor Sent to the wet oxidation reactor, the newly dissolved and easily oxidized organic compounds present might, it was reasoned, provide the source of electrons necessary for POM initiated radical-chain autoxidation of recalcitrant organic compounds left over from the previous wet oxidation cycle. This hypothesis was tested using a single solution of 2 in eight successive bleaching/wet oxidation cycles. After several cycles, a steady state was achieved in the COD values of the regenerated liquors leaving the wet oxidation reactor (Figure 4, lower plot).

The amount of carbon dioxide generated during the wet oxidation reactions remained constant throughout all eight cycles of the experiment. The achievement of a low steady state concentration of dissolved organics represents a net conversion of all organic compounds introduced to carbon dioxide and water. Assuming that the conditions of the COD test procedure (dichromate in 50% sulfuric acid at 150 °C) convert all organic compounds in the liquor samples to carbon dioxide and water, the results shown in Figure 4 demonstrate that mill closure could be achieved by using POM complexes to facilitate the wet oxidation of dissolved organic compounds. Studies designed to better understand the complex kinetics of the radical-chain reactions and the interplay of variables that lead to establishment of a steady state are in progress.

CONCLUSIONS

Data presented here demonstrate that POM complexes are able to: 1) selectively delignify unbleached kraft pulps to low kappa numbers, and 2) facilitate the complete wet oxidation of dissolved lignin fragments to carbon dioxide and water. In addition, recent studies demonstrate that POMs are quickly and easily washed from pulps. The washing data is currently being used by one industry collaborator for mathematical modelling of commercial washing. Optimization of POM delignification and bleaching reactions is underway in collaboration with industry and aided by fundamental studies concerning heterogeneous kinetics and model studies designed to elucidate the mechanism(s) of POM delignification. Progress is also being made in developing a single POM complex possessing all the requisite physical and chemical properties for optimal operation in Unit Operations A and D. Once these and related tasks have been completed, the information necessary for pilot testing of an oxygen-based, highly Selective, closed mill POM bleaching technology will be in hand.

REFERENCES


ACKNOWLEDGMENTS

The authors wish to thank the USDA Forest Service for continued support, the Shieldalloy Metallurgical Corporation for gifts of vanadyl sulfate and sodium metavanadate, and Osram Sylvania, Inc. for gifts of sodium tungstate. I.W. and K.H. acknowledge a grant from the USDA (contract no. 93-37103-9270). Additional funds and contributions-in-kind have been provided by an international consortium of pulp manufacturers and equipment suppliers.