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A new environmentally benign technology for transforming wood pulp into paper

Engineering polyoxometalates as catalysts for multiple processes

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Abstract

A new environmentally benign technology, based on the use of polyoxometalate (POM) salts and oxygen, is being developed to bleach wood pulps for use in the manufacture of paper. Details of POM chemistry relating to the unit operations of an effluent-free bleaching process are reported. These include anaerobic delignification of wood pulp, aerobic reoxidation of reduced POMs for their cyclic reuse and POM catalyzed and initiated aerobic mineralization (wet oxidation) of lignin fragments removed from pulp during bleaching. The results of bleaching trials using a series of isostructural POM complexes of the Keggin family are reported. Key structural components of the POMs are varied to determine the effects of these changes on POM performance. Homogeneous reactions of lignin-model compounds with select POMs are used to help interpret kinetic data obtained in the heterogeneous reaction of POM solutions with pulp fibers. Finally, new directions in catalyst design that promise to expand the potential of the technology are discussed.

Keywords: Polyoxometalates; Oxygen; Wood pulp; Paper; Oxidative bleaching; Oxidative delignification

1. Introduction

Some unique characteristics of the polyoxometalates (POMs) have made possible their use as the cornerstone of a new technology for the delignification of wood and wood pulp fibers. This technology promises both environmental and economic advantages over current practice in the industry. The Achilles heel of most processes currently in use is their rather

limited selectivity with respect to delignification. The most desirable condition is that a process remove the lignin, which is the primary encrustant of cell wall matter in higher plants, with little or no damage to the polysaccharides, particularly the cellulose, which is the primary substance of the cell wall and the key constituent of the natural fibers from which paper is made.

Most systems for delignification become quite aggressive, particularly as the level of lignin declines, so that delignification to desired levels

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frequently carries the penalty of some degradation in fiber properties. The goal of the program based on POMs has been to focus on their application under conditions wherein a far higher level of selectivity is achieved. A key added benefit is that the same POMs can be used in a complementary process to catalyze the wet oxidation of the organic byproducts of the delignification stage.

In this report we provide an account of the development of the POM delignification technology. We begin with some background information on wood, pulping and bleaching technology, and the lines of inquiry that led to identification of POMs as the promising candidate reagents for this work. We then describe exploratory bleaching and related studies carried out with particular POMs and ongoing developmental work. Finally, we consider new directions in catalyst design that promise to expand the potential of the technology.

2. Background

2.1. Wood

In the context of utilization technologies, wood is regarded as a material or process feedstock. In fact, it is a biological tissue that is highly organized at the cellular and molecular levels [1]. Its structural components consist pri-

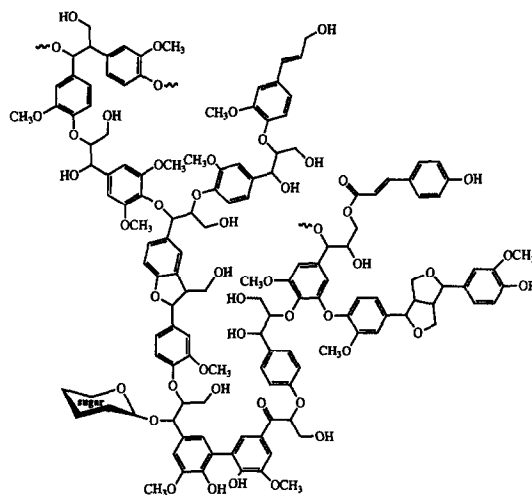


Fig. 2. Partial structural representation of softwood lignin.

marily of polysaccharides (cellulose and hemicelluloses) and lignin. Lignin, which constitutes roughly 20–35% by weight of most woods, is a highly cross-linked hydroxylated and methoxylated phenylpropane polymer formed by oxidative coupling of *para*-hydroxycinnamyl alcohols biochemically derived from the amino acid phenylalanine (Fig. 1 and Fig. 2) [2,3]. Cell division and growth are limited to the cambium layer at the outer circumference of a tree. Upon maturation, wood cells die, leaving behind rigid cell walls constructed of lamellar layers of polymeric polysaccharides. Lignin is found between cells and within the cell walls, providing both resistance to biological attack and structural

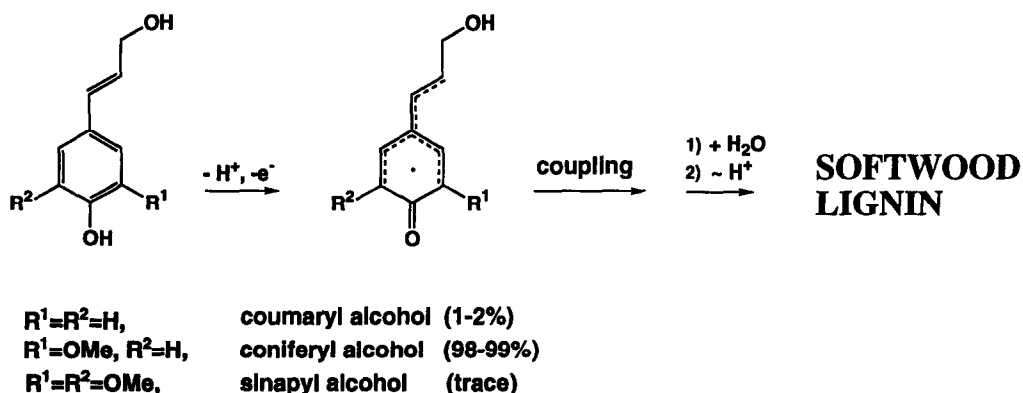


Fig. 1. Formation of softwood lignin via oxidative enzymatic coupling of *para*-hydroxycinnamyl alcohols.

rigidity. In the manufacture of paper, individual wood cells, or fibers, are separated from one another in a pulping process and then bleached. The bleached wood pulps are slurried in water and formed into thin sheets.

2.2. Pulp

Pulps can be made in two ways, either by mechanical separation of wood fibers (mechanical pulps) or by chemical removal of lignin (chemical pulps) [4]. The amount of lignin remaining in the pulp affects both the physical properties, such as strength and flexibility, and the chemical stability of the finished paper. Mechanical (high yield) pulping results in some fiber damage and a high lignin content. Such pulps are bleached using oxidative or reductive agents that remove chromophoric groups, but leave much of the lignin in the fibers, and are used for the manufacture of newsprint and lower quality paper. The ‘yellowing’ that occurs upon exposure of these products to sunlight arises from photochemical changes in the lignin component of the paper.

Chemical pulps are used for the manufacture of high strength paper products, such as cardboard, and for high quality printing and writing papers. During chemical pulping, most (but not all) of the lignin is removed. A high proportion of chemical pulps produced in the United States and in much of Europe are manufactured from conifers, such as pine, using the kraft process. Kraft pulping, which entails cooking wood chips at high temperature (ca. 170°C) in an aqueous liquor consisting of sodium hydroxide and sulfide, removes roughly 80–90% of the original lignin by nucleophilic cleavage and concomitant fragmentation and solubilization of the polymer. The remaining lignin (residual kraft lignin) is structurally distinct from native lignin. While possessing structures already present in native lignin, it is enriched in condensed structures that either survive the kraft cook (biphenyl structures) or arise from it (diarylmethane structures, Fig. 3) [5]. Approximately 20–40% of the phenyl

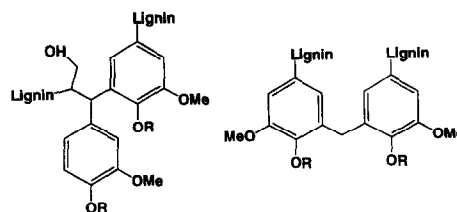


Fig. 3. Representative diarylmethane structures present in residual lignin after kraft pulping.

rings in residual kraft lignin are hydroxylated, as opposed to roughly 15% in native lignin [6]. In addition, some highly conjugated structures are generated, which, even at low concentrations, impart a dark brown color to the kraft pulp. Brown paper bags, familiar in the United States, and corrugated cardboard boxes familiar worldwide, are usually made directly from unbleached kraft pulp. However, before this pulp can be used in the manufacture of high quality, thermally and photochemically stable, white printing and writing papers, it must first be bleached. The purpose of bleaching is to chemically remove residual kraft lignin (delignification) and chromophores (brightening).

2.3. Oxidative bleaching

Delignification has traditionally been accomplished using aqueous molecular chlorine at pH 1.5–3.0 [7]. The chlorination stage (identified by the letter ‘C’) is the first step in a multi-stage process denoted CEDED where C refers to molecular chlorine, E refers to extraction with alkali and D refers to treatment with chlorine dioxide. The D stages are where brightening occurs. During the C stage, electrophilic aromatic substitution of phenyl rings in the lignin polymer generates chloroaromatic by-products which are difficult to degrade effectively in the biological waste-treatment lagoons located at mill sites [8]. For this reason, the industry in most developed countries has moved away from the use of elemental chlorine and has replaced it with a combination of extended delignification during kraft pulping, alkaline oxygen pretreat-

ment prior to bleaching and chlorine dioxide in place of elemental chlorine. Chlorine dioxide, though more costly and hazardous than chlorine, can also be used for delignification. Although it generates far fewer chlorocarbon by-products than does Cl_2 , some, however, are still produced [9].

The most attractive alternatives to chlorine and chlorine dioxide, with respect to both environmental impact and cost, are oxygen, hydrogen peroxide and ozone. The limiting issue in industrial use of these chemicals is often their intrinsic or operational (process) selectivities for lignin (vs. cellulose); high selectivity is crucial to retaining the strength properties of pulp fibers. Oxygen is the oxidant of first choice based on cost and environmental concerns. It is effective at depolymerizing and solubilizing lignin when applied under mild pressure to alkaline, aqueous pulp slurries. However, because a variety of uncontrolled autoxidation reactions occur, the process is not sufficiently selective to remove more than half of the residual lignin from kraft pulps [10]. Alkaline hydrogen peroxide, while it readily and selectively degrades chromophoric groups such as the many quinonoid compounds present in residual kraft lignin, does not delignify effectively [8]. More selective delignification is obtained using organic or inorganic derivatives such as performic or peracetic acids [8] or dioxiranes [10], persulfates [11], or peroxo-metalates [12], each of which is more expensive than hydrogen peroxide itself. In addition, the use of peroxide compounds requires the prior removal or in-situ chelation of metal ions that might otherwise lead to rapid loss of active oxidant via decomposition reactions which often proceed via unselective oxygen radical intermediates that readily degrade pulp fibers [13]. Ozone is very effective at degrading aromatic and other conjugated structures. Although the β -D-glucose units in cellulose react readily with ozone, the oxidant's relative rate of reaction with lignin is substantially greater than that with cellulose and, in principle, high selectivity is possible [10]. Mass-transfer limitations,

however, imposed by the need to deliver ozone to the dilute concentrations of lignin present within primarily cellulosic fiber walls, make high process selectivity difficult to achieve consistently on an industrial scale [14].

Ideally, a means might be found to control the action of dioxygen such that it could be used with greater selectivity. A good example is that provided by the enzymatic processes associated with the depolymerization of native lignin by wood-rotting fungi, the only micro-organisms capable of degrading this polymer. A number of extracellular metalloenzymes are involved. Laccase, a copper containing enzyme oxidizes phenolic moieties in lignin (no mono- or dioxygenase activity is reported) and reduces dioxygen directly to water [15]. In addition, two ligninolytic peroxidase systems have been described, lignin peroxidase [16] and manganese peroxidase [17]. The hydrogen peroxide needed by these enzymes is produced from simple aldehydes and dioxygen by a second copper containing enzyme, glyoxal oxidase [18]. When oxidized, lignin peroxidase, a protoheme containing enzyme, oxidizes phenolic groups and, more significantly, generates radical cations from a wide variety of non-hydroxylated phenyl structures. The second protoheme containing peroxidase, manganese peroxidase, oxidizes Mn^{II} to Mn^{III} which is stabilized at or near the enzyme active site by complexation with α -hydroxy acids. Chelated Mn^{III} ions penetrate the wood-cell wall and oxidize phenolic groups within the lignin. These systems demonstrate that delignification can be brought about by non-substrate specific, transition-metal catalyzed oxidation reactions. This observation suggests a role for molecular catalysis in the search for new, environmentally benign and economically viable bleaching technologies.

In general, however, the behavior and reactivity of transition-metal ions in water are difficult to control [19]. Complex equilibria are established between ionic oxides, hydroxides and hydrates, as well as between accessible oxidation states of the metal ions, each of which may

react in unique ways with substrates or oxidants. In addition, many transition-metal oxides and hydroxides have limited solubilities in water and the metal ions are rapidly lost from solution as solid precipitates. With the fungal peroxidases as a model, biomimetic bleaching systems have been developed using halogenated, water-soluble metalloporphyrin complexes [20]. While elegant and relatively robust structural mimics of lignin peroxidases, these synthetic materials are expensive, require the use of expensive organic or inorganic peroxides and are inherently susceptible to oxidative degradation during bleaching. An alternative approach is to control the behavior and reactivity of redox-active metal ions by incorporating them into the structures of polyoxometalate anions.

2.4. Polyoxometalates

Early transition metal oxygen anion clusters, or polyoxometalates (POMs for short) are a large, structurally diverse and rapidly growing class of inorganic clusters. They are composed of d^0 metal cations, and in particular W^{VI} , Mo^{VI} , and V^V , in varying combinations, and oxide anions held together with metal oxygen bonds [21–31]. The principal building blocks of POMs are MO_x , $x = 4–6$, polyhedra and usually MO_6 octahedra that are linked together by

one, two, and occasionally three oxygen atoms. There are two generic classes of POMs, the isopolyanions, that can contain only the d^0 metal cations and oxide anions (general formula: $M_xO_y^{n-}$), and the heteropolyanions, that contain one or more d or p block ‘heteroatom’ cations, X^{n+} , in addition to the metal cations and oxide anions (general formula: $X_aM_bO_c^{m-}$). The heteropolyanions are the focus of the research elaborated in this paper as they are a larger, more versatile, and more easily modified class of POMs than the isopolyanions [21]. The most common and most thoroughly investigated class of heteropolyanions are the Keggin structures (Fig. 4). While POMs can range in size from 9 Å (0.9 nm) to over 30 Å (3 nm), the Keggin structure has a diameter of ca. 1.1 nm, similar to that of typical phenylpropane units in lignin. The negative charge of a POM can be counterbalanced by hydrophilic cations, such as Li^+ , Na^+ , K^+ , and NH_4^+ , that render the complex soluble in H_2O , or by hydrophobic cations, such as Et_4N^+ or Ph_4P^+ , that render the complex soluble in organic solvents and other hydrophobic media.

Several attributes make POMs attractive in general and other attributes make them attractive for the bleaching and processing of wood pulp in particular. First, POMs are readily prepared, often in a single step in H_2O from

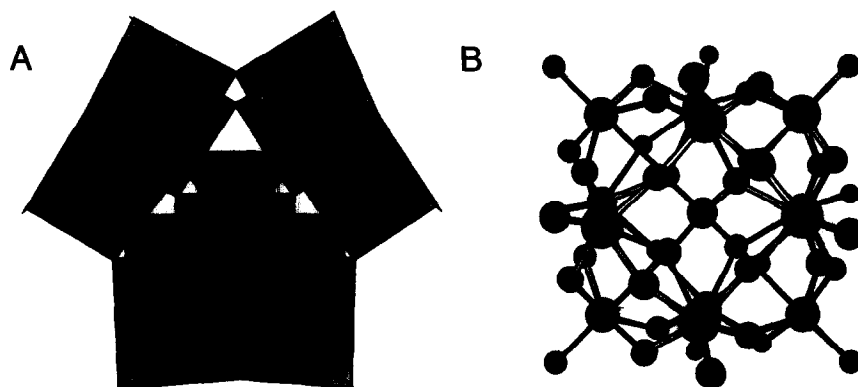


Fig. 4. The Keggin POM structure, $X^{n+}M_{12}O_{40}^{(8-n)-}$, in polyhedral (A) and ball-and-stick (B) representations. M is primarily W^{VI} or Mo^{VI} (see text); the heteroatom, X , resides in a central tetrahedral hole (the XO_4 unit partially shown in the darkest color in A, closely approximates T_d symmetry). In polyhedral notation the MO_x units are depicted; the metal ion resides in the middle of each unit and is hidden from view; the vertices are the nuclei of the oxygen atoms.

inexpensive, minimally toxic, and accessible compounds such as WO_4^{2-} , MoO_4^{2-} , and PO_4^{3-} [21–31]. Second, most of the key physical properties of POMs that control their fundamental reactivities including redox potentials, acidities, charges, solubilities, etc. can be controlled to a marked degree by choice of precursors and conditions. It is doubtful if another class of compounds exists whose properties can be so extensively and so readily altered. Third, and a point of particular pertinence to the title technology, POMs are simultaneously resistant to oxidation (such d^0 systems as glass, some ceramics and other inorganic materials are already in the maximum oxidation state achievable under any conventional reaction conditions), yet many families of POMs, including Keggin derivatives, can be reversibly reduced, often by many electrons. Finally, one or more of the d^0 metal ions in the parent POM structure can be replaced by other d^0 metal ions or by d-electron-containing metal ions. Indeed, the profound control of the chemically significant properties of POMs enumerated above vests, in part, in this rich substitution chemistry. These metal-ion substituted POMs can remove electrons from organic substrates such as lignin and facilitate their transfer to O_2 . As such, they perform the same function as do the extracellular enzyme systems of wood-decay fungi. The POMs addressed in the initial research elaborated in this paper are Keggin derivatives with P^{V} , Si^{IV} , or B^{III} heteroatoms and with one or more W^{VI} or Mo^{VI} ions substituted with V^{V} (d^0) or d-electron-containing (e.g. Mn^{III}) ions.

3. POM bleaching

The POM bleaching process now being developed at the US Department of Agriculture Forest Service, Forest Products Laboratory, in collaboration with the Emory University, Department of Chemistry and the University of Wisconsin–Madison, Department of Chemical Engineering, uses a highly selective and com-

pletely reusable POM bleaching agent [32–40]. In bleaching, fully oxidized POM complexes are reacted with unbleached pulp under anaerobic conditions. During bleaching, the POM complexes are reduced and oxidized lignin fragments dissolved by the bleaching liquor. Because the POM bleaching complexes are reversible, and thus reusable, oxidants, designed to circulate continuously in the mill, the build-up of dissolved organic compounds must be avoided. This is accomplished by reoxidizing (reactivating) the reduced bleaching liquors with dioxygen under conditions that will convert the dissolved lignin fragments to carbon dioxide and water [33,36–40]. Thus, an effluent-free (closed mill) bleaching process, a stated goal of the pulp and paper industry, will be achieved [41].

3.1. Closed-mill POM bleaching process

As currently envisioned, an effluent-free (closed) POM 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, POM catalyzed and/or initiated, wet oxidation of dissolved lignin fragments with simultaneous regeneration of the POM to its bleaching-active form (Fig. 5).

In anaerobic bleaching, (unit operation A, Fig. 5) the POMs are dramatically more selec-

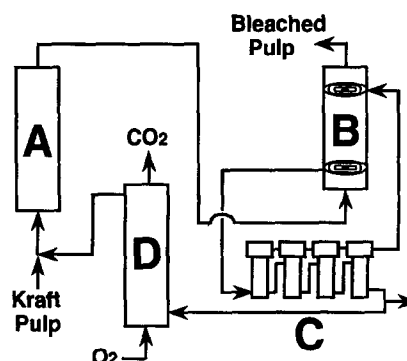
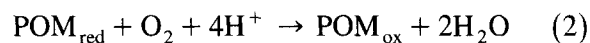
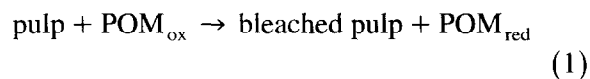


Fig. 5. Simplified schematic of an effluent-free POM bleaching process (see text).

tive than molecular oxygen and yet, many have the attractive property that after use in bleaching, the now reduced POMs are thermodynamically capable of being reoxidized by oxygen (unit operation D). Bleaching and the regeneration of used bleaching liquors are each carried out in separate steps. In the bleaching step (represented in Eq. (1)) mixtures of water, pulp and a fully oxidized polyoxometalate (POM_{ox}) are heated anaerobically. During the reaction, the POM is reduced (POM_{red}) 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). By separating aerobic reoxidation of POM_{red} from anaerobic bleaching, oxygen can be utilized as a terminal oxidant while avoiding exposure of the pulp to non-specific oxygen radicals. Because the POMs only serve in a mediating role for oxygen, water is the only by-product of the bleaching chemicals.



After leaving the bleaching reactor, the pulp is washed (unit operation B, Fig. 5). Because the POMs are not adsorbed onto pulp fibers, their removal is controlled by diffusion phenomena alone. As a result, the POMs are easily washed out of the pulp. Industrially, a series of countercurrent washers would be used. Wash water would be recycled by evaporation using heat provided by low grade steam, which is often abundantly available in pulp mills. 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). 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 (Fig. 5), 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. 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 metalloporphyrins are susceptible to oxidative degradation. Upon cessation of the wet oxidation reactions, the liquor, now containing active POM_{ox} , is returned to the bleaching reactor.

4. Experimental

4.1. Analytical methods

The kappa number of a wood pulp is a standard pulp and paper industry index of its lignin content. Kappa numbers are determined by measuring the extent to which a standardized solution of permanganate is reduced when vigorously mixed with a pulp sample at a given temperature for a given time. Weight-percent lignin in pulp is empirically determined to be (0.15) (kappa number). Kappa numbers of unbleached kraft pulps vary from approximately 20 to 35 (3.00–5.25% lignin). Microkappa numbers (obtained from relatively small pulp samples) were determined using Technical Association of the Pulp and Paper Industry (TAPPI) useful method um-246 [42]. Pulp viscosity, a non-linear function of the degree of polymerization of the cellulosic component, is an indirect measure of the extent to which fibers have been damaged by degradation of individual cellulose chains. Viscosity measurements were obtained, using a capillary viscometer, from solutions of

pulp samples in aqueous solutions of ethylenediamine and cupric sulfate, a good solvent system for dissolution of cellulose (TAPPI test method T230 om-89) [43]. Viscosities of unbleached kraft pulps are generally near 30 mPa s and those of market-grade bleached pulps range from roughly 18–25 mPa s. Routine ^{31}P and ^{51}V NMR spectra were obtained on a 250 MHz Bruker instrument according to published methods and externally referenced to H_3PO_4 and VOCl_3 , respectively [44]. Reduction of POMs was measured by titration with Ce^{IV} in 0.1 M H_2SO_4 or by UV–vis spectroscopy.

4.2. Materials

Two unbleached mixed-pine kraft pulps, one with a kappa number of 33.6 and a viscosity of 34.2 mPa s (pulp 1) and one with a kappa number of 24.1 and a viscosity of 27.8 mPa s (pulp 2) were supplied by Consolidated Papers, Wisconsin Rapids, WI. Bleaching, wet oxidation and model studies were performed using salts of the α -Keggin anions (all shown here in their POM_{ox} forms): α - $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ (**1**) [45], $[\text{V}_{10}\text{O}_{28}]^{6-}$ (**2**) [46], α - $[\text{PVW}_{11}\text{O}_{40}]^{4-}$ (**3**) [47], α - $[\text{SiVW}_{11}\text{O}_{40}]^{5-}$ (**4a**) [48], α - $[\text{BVW}_{11}\text{O}_{40}]^{6-}$ (**5**) [49], in which $\text{V}=\text{V}^{\text{V}}$, and α - $[\text{SiMn}^{\text{III}}(\text{OH}_2)\text{W}_{11}\text{O}_{39}]^{5-}$ (**6**) [50]. Compound **1** is prepared as an equilibrium mixture of α - $\text{Na}_x\text{H}_{4-x}[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$, α - $\text{Na}_x\text{H}_{5-x}[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ and α - $\text{Na}_x\text{H}_{6-x}[\text{PV}_3\text{Mo}_9\text{O}_{40}]$ in which the divanadium species is favored and where the ratios $x/(4-x)$, $x/(5-x)$ and $x/(6-x)$ are determined by pH [51]. In addition, in the di- and trivanadium complexes, positional isomers are present. Henceforth, this mixture of compounds, in which **1** and its positional isomers dominate, will be referred to as compound **1**. The one-electron reduced form (V^{IV} , POM_{red}) of compound **4a** was prepared by stoichiometric addition of VOSO_4 to a solution of α - $\text{K}_8[\text{SiW}_{11}\text{O}_{40}]$, obtained as described in Ref. [48]. The solution was then filtered and cooled to collect dark purple crystalline α - $\text{K}_6[\text{SiVW}_{11}\text{O}_{40}]$ **4b**. The

one-electron reduced forms of compounds **4a**, **5** and **6** were oxidized in aqueous solution by sparging with ozone at room temperature. In the preparation of **4a**, a stoichiometric amount of sulfuric acid was added prior to ozonation (one equivalent of hydroxide is formed per electron-equivalent of V^{IV} oxidized). Ozonation of **5** and **6** was carried out in the presence of pH 5 acetate buffer. Solid products were obtained by crystallization of the acid (**1**), sodium salt (**2**) or potassium salts (**4a–6**) and were characterized by FTIR (KBr pellet), ^{31}P and ^{51}V NMR spectroscopies. Solutions of **3** were prepared prior to use by direct acidification of stoichiometric combinations of phosphoric acid, sodium metavanadate and sodium tungstate, a method known to give exclusively **3** [47]. The acid of **3** was the only phosphorus-containing product observed by ^{31}P NMR in these solutions. Compound **6** was characterized by FTIR, UV–vis and by titration to a starch endpoint using potassium iodide and sodium thiosulfate.

4.3. Bleaching reactions

4.3.1. $\text{H}_5[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$ (**1**); M_{O} and M sequences

A series of reactions were performed using **1** at several pH values and under both aerobic (M_{O}) and anaerobic (M) conditions, using the following general method. Pulp 1, obtained as a 30% solids mass of hydrated pulp fibers (30% consistency or csc), was combined with an 0.054 M solution of **1** to obtain a 3% csc mixture of pulp fibers in a 0.05 M solution of **1**. The solution was adjusted to the desired pH by addition of small amounts of either concentrated H_2SO_4 or aq NaHCO_3 and the mixture was placed in a 2 l Parr reactor and purged with purified nitrogen, while stirring, for 30 min. The reactor was then sealed under nitrogen and heated to 100°C for 4 h. During the reaction, aliquots of the POM solution were removed and the extent of reduction of the vanadium from V^{V} to V^{IV} was determined by titration with Ce^{IV} to a yellow endpoint. The pulps were then

washed thoroughly with water in a Büchner funnel. Alkaline extraction (E) was performed by heating the pulp at a csc of 3.2% at 85°C under nitrogen for 3 h in 0.25 to 1.0 M NaOH. In experiments where oxygen was used (M_O stages), the pulps slurried in POM solutions were purged with purified O_2 gas and then heated under dynamic O_2 pressures of 1.0 atm. After reaction, no reduction of the POM solutions was observed. After anaerobic bleaching trials, moist air was bubbled gently through reduced POM solutions for 1.5 h at 60°C, and the pH values of the solutions were then adjusted to 1.5 with concentrated H_2SO_4 . The reoxidation was monitored spectrophotometrically at 756.9 nm (fully reduced solutions are deep blue, fully oxidized ones are orange). After reoxidation, ^{31}P NMR spectra of the used POM solutions were obtained. No phosphorus-containing decomposition products were observed. Control experiments were carried out under identical conditions but with no POM added. In some cases, an acid pretreatment was used to remove metal ions from the pulp prior to bleaching. In such cases, the pulp was soaked for 15 min in a cold solution of 0.5 wt% H_2SO_4 at a csc of 8.3% and rinsed thoroughly with distilled water.

4.3.2. $Na_6[V_{10}O_{28}]$ (2); ME sequence

Pulp 1 (0.10 g odw) was added to a 0.10 M solution of compound 2 to a final csc of 2.7% in a 15 ml round-bottomed flask. The pH of the mixture was adjusted to 2.5 with concentrated H_2SO_4 . Air was removed in three freeze-pump-thaw cycles, and the flask was sealed under purified nitrogen and heated in a 100°C bath for 4 h. During heating, the solution changed from orange to red-brown and precipitate of the same color fell out of solution. The mixture of pulp and precipitate was collected on a Büchner funnel and washed with water. Little if any of the precipitate dissolved. The pulp was soaked for 3 h at room temperature in 1 M NaOH to dissolve the precipitated vanadates, washed with water, and extracted for 3 h at

85°C in 1.0% aqueous NaOH. Little delignification was observed [36].

4.3.3. $\alpha-H_4[PVW_{11}O_{40}]$ (3); M_OE sequence

Pulp 1 (1.0 g odw) was added to a 0.09 M solution of compound 3 to a final csc of 3.0% in a 100 ml round-bottomed flask. The pH of the mixture was adjusted to 1.50 with concentrated H_2SO_4 . The flask was sealed in air (the reduced form of 3, $\alpha-H_5[PVW_{11}O_{40}]$ reacts very slowly, if at all, with dioxygen) and immersed in a 100°C oil bath for 4 h (average reaction temperature was approximately 95°C). During heating, the solution changed from orange to greenish-brown. The pulp, now somewhat lighter in color, was collected on a Büchner funnel and the partially reduced polyoxometalate solution (pH 1.67) was saved. After reaction, 43.6% of the vanadium was present as V^{IV} . The pulp was washed three times with water and heated for 3 h at 85°C in 0.25 M aqueous NaOH at a csc of 3.2% in an open round-bottomed flask. At the end of this time the alkali solution was brown, and the pulp was lighter in color. ^{31}P NMR spectra of used POM solutions were obtained after reoxidation by oxone (a potassium monopersulfate compound, DuPont). Phosphorus-containing products of rearrangement or disproportionation were observed at concentrations of less than ca. 5.0%. These signals have been tentatively assigned to isomers of $Na_5[PV_2W_{10}O_{40}]$. No other phosphorus-containing compounds were observed.

4.3.4. $\alpha-K_5[SiVW_{11}O_{40}]$ (4a); $M_1M_2M_3E$ Sequence

To model a continuous countercurrent process and to follow the course of the bleaching reactions, POM treatments of unbleached pulp were divided into three successive batch reactions, M_1 , M_2 and M_3 . In the first set of bleaching trials, pulp 1 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. M stages were run in stirred, glass-lined, 1 or 2 l high pressure

Parr reaction vessels. The pulps were slurried at 3% csc in bright yellow 0.05 M solutions of $\alpha\text{-K}_5[\text{SiVW}_{11}\text{O}_{40}]$ (**4a**) in 0.2 M pH 7 potassium phosphate buffer. After purging with nitrogen, the reactor was heated to 125°C (ramp time of 40 min) and held at temperature one h for M_1 , and 2.0 h for M_2 and M_3 . The reactor pressure was sustained with nitrogen at ca. 50 psig. During bleaching, the pH slowly decreased from seven to no lower than six. The liquor changed from a bright yellow color of fully oxidized **4a** to the dark purple of its one-electron reduced form, $\alpha\text{-K}_6[\text{SiVW}_{11}\text{O}_{40}]$ (**4b**). After each batch reaction the pulps were collected in a Büchner funnel and washed three times with water. A parallel control sequence was performed by heating mixtures of pulp, water and phosphate buffer in three successive batch reactions but with no POM present. Both sequences were followed by anaerobic extraction with 1% NaOH for 2 h at 85°C with pulp consistencies of 1–2%. In addition, two samples of the unbleached pulp were each partially delignified using elemental chlorine followed by extraction with alkali (CE). In the first case, 7.4% chlorine, $100 \cdot (\text{weight of Cl}_2 / \text{dry weight of pulp})$, was applied to the unbleached pulp, and 9.0% chlorine was applied to a separate sample of the unbleached pulp. For determination of paper-making properties, a POM delignified pulp was compared to a pulp delignified using a (C/D)E sequence. Due to an insufficient supply of pulp 1, a similar pulp, 2, was used. This pulp was delignified in triplicate runs using batch POM ($M_1M_2M_3E$) sequences as described above and by a (C/D)E sequence (a mixture of Cl_2 and chlorine dioxide in which 30% of the total oxidative equivalents present are supplied by ClO_2), which provided a delignified pulp close in kappa number to the POM delignified pulp [7]. A POM-free control was performed once.

4.3.5. Kinetic studies using $\alpha\text{-K}_5[\text{SiVW}_{11}\text{O}_{40}]$ (**4a**)

Data used for kinetic modeling were obtained during a $M_1M_2M_3$ sequence carried out as

reported above, but at 130 rather than 125°C. In addition, a single-M-stage experiment was performed using untreated pulp 2 according to the procedure described immediately above, except that the reaction was run at 100°C for 4 h. Progress of reaction was followed by measuring, either titrimetrically or by UV-vis spectroscopy (496 nm), concentrations of the one-electron reduced anion $\alpha\text{-}[\text{SiVW}_{11}\text{O}_{40}]^{6-}$ (**4b**). Concentrations of unreacted **4a**, $[\text{POM}_{\text{ox}}]$, (as $[\text{POM}_{\text{total}}] - [\text{4b}]$) were used in the kinetic model. In addition, kappa numbers, obtained after each batch reaction, were mathematically treated as indicating lignin concentrations, [lignin]. These data are presented in Fig. 13 and Fig. 14.

4.3.6. NMR evaluation of the stability of $[\text{BVW}_{11}\text{O}_{40}]^{6-}$ (**5**) in carbonate buffer

All NMR spectra were recorded on a General Electric GN 500 spectrometer. The ^{51}V chemical shifts were referenced to HVO_4^{2-} in water, ^{11}B shifts were referenced to NaBH_4 in water; referencing was achieved by the substitution method. Chemical shifts downfield from the reference are reported as positive (+ δ). In reporting NMR data, multiplicity and line widths (in Hz), as applicable, are given in parentheses. The probe temperature was 295 K in all NMR experiments. The spectral parameters for ^{51}V NMR were acquisition time = 106.5 ms, relaxation delay = 300 ms, pulse width = 15.0 μs , spectral window = 38462 Hz, digital resolution = 2.35 Hz/point. The spectral parameters for ^{11}B NMR were acquisition time = 204.8 ms, relaxation delay = 1.50 s, pulse width = 15.0 μs , spectral window = 20000 Hz, digital resolution = 1.22 Hz/point.

4.3.7. Effect of carbonate buffer, pH and oxidation state of vanadium in **5**

Four 200 mg portions of **5** were each dissolved in 2.0 ml of 0.10 M aqueous carbonate buffer. Two samples were prepared at pH 7.0 and two at pH 8.5. One sample at each pH value was reduced with 1.0 eq of hydrazine and all

four were maintained at 25°C for 18 h. Two additional samples of **5** (200 mg) were prepared in pure water (2.0 ml) without buffer. One of these was adjusted to pH 8.5 using dilute aq NaOH, the other was first reduced with hydrazine and then adjusted to pH 8.5, and both were refluxed for ca. 1.5 h. Reduced samples were reoxidized with a slight excess of Br₂ and all six were analyzed by ⁵¹V NMR.

4.3.8. α -K₅[SiMn^{III}(OH₂)W₁₁O₃₉] (**6**); M₁M₂M₃E sequence

For the M₁ stage, pulp 1 was added to a solution of **6** in 0.20 M pH 5 potassium acetate buffer to give a final csc of 3% and a POM concentration of 0.05 M. The pH after mixing was 5.02. The mixture was then placed in a glass lined Parr high pressure reactor and, while stirred, was purged with purified nitrogen for 40 minutes, sealed, and heated to 125°C for 1 h. During this time, the pH of the POM solution dropped to 4.86. The POM bleaching liquor was then recovered by filtration and the pulp washed with water. The amount of **6** reduced to α -K₆[SiMn^{II}(OH₂)W₁₁O₃₉] (**7**) during the bleaching reaction (M₁ stage) was determined by reaction of an aliquot of the bleaching liquor with an excess of potassium iodide and titration to a starch endpoint with sodium thiosulfate. Over the course of the bleaching reaction, more than 98.9% of the salt **6** present had been reduced to **7**. Upon cooling the bleaching liquor to 0°C for three days, ca. 50% of orange crystalline **7**, characterized by FTIR (KBr pellet), was recovered. The UV–vis spectrum of the supernatant was consistent that of a mixture of **6** and **7**. During the M₂ stage (1.5 h) the pH dropped from 5.14 to 4.95 and 89.2% of the POM present was reduced. The M₃ stage was run for 2 h during which the pH dropped from 5.16 to 4.89 and 66.8% of the POM present was reduced. After the three sequential M stages, an alkaline extraction (E) was performed as described above. A control experiment was performed by subjecting pulp to the same procedure, but with no POM present. Oxidation of **7**

at pH 5 by oxygen, at elevated temperature and O₂ pressure, is slow.

4.4. Wet oxidation of dissolved organics (unit operation D)

Eight bleaching-wet oxidation cycles, each consisting of an anaerobic bleaching reaction followed by an aerobic wet oxidation reaction of the spent bleaching liquor, were carried out using a single solution of **1**. The bleaching was done using kraft pulp 2 at 3% csc. The POM liquor was maintained at a concentration of 0.05 M for both the bleaching and wet oxidation reactions through the evaporation or addition of water as necessary. A pH of 3 was maintained by periodic addition of small amounts of dilute sulfuric acid. Bleaching was carried out in a stirred high pressure Parr reaction vessel with a glass liner at 100°C for 4 hrs under nitrogen. Kappa reductions of 5 were typical. The dark green reduced liquor (typically 14–17% of the total vanadium present was reduced to V^{IV}) 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 wet oxidation reaction was performed 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 h under an oxygen pressure of 100 psig. 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 chemical oxygen demand (mg O₂/l, COD) of the liquors were measured. Carbon dioxide was measured by acid–base titration of aqueous Ba(OH)₂ solutions through which reaction vessels were vented after completion of bleaching or wet oxidation reactions [52]. Prior to each venting, a Ba(OH)₂ solution, prepared under nitrogen, was placed in a chromatography column. Gases were introduced from the bottom through a glass frit using inert atmosphere tech-

niques to avoid contamination with atmospheric CO_2 . Small amounts of isopropanol were added to the $\text{Ba}(\text{OH})_2$ solutions to promote foaming, thus increasing gas–liquid contact. For purposes of comparison, carbon dioxide values are reported as $\text{mg CO}_2/(\text{l of POM liquor present in the reaction})$. COD determinations were carried out by exhaustive oxidation of POM liquors accomplished by adding c. H_2SO_4 (a volume equal to the volume of the aqueous sample being tested) and an excess of potassium dichromate and heating to reflux (ca. 150°C) for several hours [53]. The extent of dichromate reduction was then determined by titration with ferrous ammonium sulfate using a ferroin indicator. For bleach liquors containing reduced **1**, the concentrations of V^{IV} ions present prior to dichromate oxidation were accounted for in the calculation of COD values. The integrity of **1** after completion of the 8 bleaching–wet oxidation cycles was confirmed by ^{31}P NMR spectroscopy.

5. Results and discussion

5.1. Physical properties of POM bleaching catalysts

POM salts useful in the present context must be reversible oxidants, capable of undergoing repeated cycles of reduction and reoxidation without degradation. In addition, their oxidized forms, POM_{ox} , must have reduction potentials sufficiently positive to oxidatively degrade lignin, while, at the same time, sufficiently negative such that reoxidation with dioxygen is possible. Using lignin model compounds, we have found that POM bleaching occurs via oxidation of phenolic moieties in residual lignin and that non-hydroxylated phenyl rings, including those possessing α -alcohol substituents (benzylic alcohols), react too slowly to contribute significantly to delignification. Thus, the POM reduction potentials necessary for delignification are those needed to oxidize phenolic

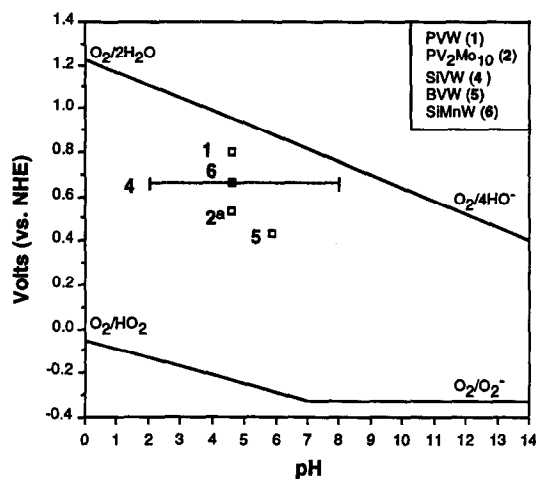


Fig. 6. Reduction potentials of several POM salts used in the present study, and of those for the one and four-electron reductions of dioxygen, as a function of pH. Values for compounds **1** and **5** were reported in Ref. [49], the value for **6** was obtained from ref. 50 and the values for **4** are from this work. ^a Estimated value based on data published in Ref. [49].

structures. In Fig. 6, the reduction potentials of several of the POM salts used in the present study are shown in relation to those for four-electron reduction of dioxygen as a function of pH. All POM complexes whose reduction potentials lie below that of dioxygen, and are at the same time positive enough to oxidize phenolic groups in lignin, are thermodynamically capable of transferring electrons from lignin to oxygen. This is the same task accomplished by the extracellular ligninolytic metalloenzyme systems of wood-rotting fungi.

Another practical consideration in pulp bleaching is the need to avoid hydrolysis of pulp fibers that occurs most readily at elevated temperatures, such as those encountered in POM bleaching. This hydrolysis is due to the acid-catalyzed cleavage of glycosidic linkages in cellulose. At very high pH values, alkaline degradation reactions can occur and the optimal pH range for avoiding either cellulose hydrolysis or degradation (acid catalyzed or alkaline) is near 9–10. This, combined with the knowledge that POM bleaching occurs via phenol oxidations, leads to the possibility that optimal rates and effectiveness might be observed near pH values

of 9–10, which correspond both to the range of pK_a values of many phenols and to the pH region in which the least amount of cellulose hydrolysis is expected to occur at elevated temperatures.

In general, tungsten(VI, d^0)-based POMs are less labile, more stable to alkaline hydrolysis and possess higher reduction potentials than their isostructural and isoelectronic molybdenum(VI, d^0) analogues. For example, the α -[PV₂Mo₁₀O₄₀]⁵⁻ anion (**1**) is stable to a pH of 3.5 to 4.0, while the isoelectronic tungsten analog, α -[PV₂W₁₀O₄₀]⁵⁻ is stable to a pH of near 5 [54]. Also, within the Keggin structural class, increases in anion charge density are associated with greater resistance to alkaline hydrolysis and with increasingly negative reduction potentials. In the series α -[PVW₁₁O₄₀]⁴⁻ (**3**), α -[SiVW₁₁O₄₀]⁵⁻ (**4a**) and α -[BVW₁₁O₄₀]⁶⁻ (**5**), whose charge increments follow the decrease in positive charges of their central, tetrahedrally coordinated heteroatoms, P^V, Si^{IV} and B^{III}, hydrolytic stabilities increase with increasing negative charge density. The tungstophosphate anion, **3**, is stable perhaps to a pH of 3, while **4a**, and its one-electron reduced form α -[SiV^{IV}W₁₁O₄₀]⁶⁻ (**4b**) are stable indefinitely at reflux in water at pH 7. The hydrolytic stability of the tungstoborate compound, **5**, was determined by potentiometric titration at 80°C of a 2.0 mM solution of **5** with dilute aqueous sodium hydroxide. These preliminary data suggest that the anion is stable up to a pH range of approximately 8.5–9.5. At the same time, it has been observed that the reduction potentials of fully deprotonated Keggin anions (i.e., their sodium salts) in water decrease linearly with anion charge [49] (compare for example **1**, **4** and **5** in Fig. 6).

The standard electrode potential for the V^V/V^{IV} couple in 1.0 M acid is +1.00 V versus the normal hydrogen electrode (NHE). The potentials of vanadium-containing POMs useful in the present context likely lie in the range 0.4–0.8 V. This range might be compared to the standard reduction potentials of several

other oxidants used to delignify pulp: acid O₃ (+2.07 V at pH 0, O₃ + 2H⁺ + 2e⁻ → O₂ + H₂O), acid Cl₂ (+1.36 V at pH 0, Cl₂ + 2e⁻ → 2Cl⁻), acid ClO₂ (+1.27 V at pH 0; ClO₂ + H⁺ + e⁻ → HClO₂), alkaline H₂O₂ (+0.87 V at pH 14, HO₂⁻ + H₂O + 2e⁻ → 3OH⁻) and alkaline O₂ (+0.402 V at pH 14; O₂ + 2H₂O + 4e⁻ → 4OH⁻) [55,56]. Of these, the best comparisons are with acid ClO₂ and alkaline O₂, both of which delignify to a significant extent via single-electron oxidations of phenol or phenolate lignin substructures [57].

5.2. Bleaching trials

A broad survey of POM bleaching effectiveness was undertaken using vanadium(V)-substituted POM salts possessing P^V, Si^{IV} and B^{III} heteroatoms. The results are reported here as follows. First, results obtained using a molybdophosphate, α -[PV₂Mo₁₀O₄₀]⁵⁻ (**1**), are reported. For comparison, a general control experiment was performed using aqueous V^V cations alone, in the form of the decavanadate anion [V₁₀O₂₈]⁶⁻ (**2**). This is followed by results obtained using the series of isostructural tungsten compounds α -[PVW₁₁O₄₀]⁴⁻ (**3**), α -[SiVW₁₁O₄₀]⁵⁻ (**4a**) and α -[BVW₁₁O₄₀]⁶⁻ (**5**), possessing P^V, Si^{IV} and B^{III} heteroatoms. Next, the effectiveness of α -[SiMn^{III}(OH₂)W₁₁O₃₉]⁵⁻ (**6**), is compared to that of its analog of similar charge, **4a**. Finally, the discussion of bleaching results closes with a discussion of preliminary data pertaining to the kinetics and mechanism of delignification by **4a**.

5.2.1. α -[PV₂Mo₁₀O₄₀]⁵⁻ (**1**)

Early bleaching trials were performed using POM salt mixture **1**, which is stable only at acid pH values. This POM was chosen based on literature reports that it oxidizes phenols rapidly, that its reduced forms are readily reoxidized by dioxygen in water and that, in organic solvents, it also oxidizes 1-phenylethanol (a non-phenolic benzyl alcohol) to acetophenone, but not 2-phenylethanol, an aliphatic alcohol, the latter

implying low reactivity with β -D-glucose rings in cellulose [58]. Using **1** under aerobic conditions, extensive delignification was observed (entries 7–10, Table 1). However, pulp quality was extremely poor, probably due to the generation of unselective oxygen-centered radicals. In control experiments (entries 8 and 10, Table 1), metal ions present in the pulp and which might participate in autoxidation reactions during aerobic bleaching (namely manganese salts and iron oxide particles, both present in ca. 50–100 ppm quantities in kraft pulp) were largely removed by pre-soaking the pulp in cold dilute H_2SO_4 [59]. Subsequent aerobic POM bleaching gave results similar to those obtained using non-acid-treated pulps (entries 7 and 9, Table 1). This was strong evidence that the observed drops in viscosity were due to reactions of oxygen with reduced **1**, and not exclusively to radical-chain autoxidation processes initiated by trace metals. This led to the conclusion that, in order to maximize the selectivity achievable using POM oxidants, the bleaching reactions would have to be run anaerobically.

Under anaerobic conditions, substantial delignification occurred but with less fiber degradation than was observed in the aerobic reactions

(entries 1–6, Table 1). Nevertheless, drops in pulp viscosities were substantial, particularly at lower pH values (entries 1 and 2). However, even in organic solvents, where salts of **1** are expected to be more highly ion-paired and to thus possess higher reduction potentials than in water, no oxidation of secondary alcohols by **1** was observed [58]. Therefore, it appeared likely that pulp degradation was due primarily to acid-catalyzed cellulose hydrolysis and that optimization of the bleaching reactions would require moving to higher pH values. At the same time, because the reduction potential of **1** becomes more positive at lower pH values, this hypothesis could not be proven until a POM salt stable over a higher pH range was tried.

5.2.2. $[V_{10}O_{28}]^{6-}$ (**2**)

Meanwhile, a control was performed using V^V ions alone, in the form of $[V_{10}O_{28}]^{6-}$ (**2**), the dominant V^V -containing species present at the pH and concentration used (pH 2.5, 1.0 M V^V or 0.1 M **2**) [60]. During the reaction a large quantity of red-brown precipitate formed that was only dissolved by soaking the pulp for several hours in 1 M NaOH. Similarly, a dark green insoluble precipitate formed when dilute

Table 1
Delignification of unbleached kraft pulp by α - $[PV_2Mo_{10}O_{40}]^{5-}$ (**1**)^a

Entry No.	[1] (M)	P_{O_2} (atm) ^b	pH _O	pH _f	%V reduced ^c	Kappa No.	Viscosity (mPa s)
1	0.05	0.0	1.50	2.01	39.8	14.0	4.1
2	0.05	0.0	2.02	2.50	36.8	16.4	6.4
3	0.05	0.0	2.51	2.74	^e	18.2	14.0
4	0.05	0.0	3.01	3.05	19.2	22.3	16.9
5	0.05	0.0	3.95	4.00	26.8 ^f	25.6	25.5
6	0.00	0.0	4.05	3.95	–	28.6	23.7
7	0.05	1.0	4.03	4.10	0.0	10.2	9.5
8	0.05 ^d	1.0	4.05	3.52	0.0	10.2	8.8
9	0.00	1.0	4.02	4.47	–	19.7	15.2
10	0.00 ^d	1.0	4.00	3.70	–	20.7	15.7

^a Initial pulp (pulp 1) kappa No. and viscosity values were 33.6 and 34.2 mPa s. Kappa Nos. and viscosities reported here were obtained after alkaline extraction of pulp samples. Reaction conditions are as described in the experimental section.

^b In anaerobic trials, pulps slurried in solutions of **1** were stirred for 0.5 h under a stream of purified N_2 at room temperature in sealed Parr reactors prior to heating.

^c Total vanadium concentration = 0.10 M.

^d Pretreated with cold H_2SO_4 (see experimental section).

^e Data not available.

^f Purged for 1 h with N_2 prior to heating.

sodium metavanadate NaVO_3 solutions were used under aerobic conditions. Notably, however, throughout the series of experiments carried out using **1**, no vanadium precipitation was observed and ^{31}P NMR spectra of spent bleach liquors reoxidized by dioxygen showed no signs of POM degradation, although positional isomerization was seen. These observations stress the importance of controlling the speciation of transition metal ions in water and of providing ligand environments that ensure the reversibility of electron-transfer processes.

5.2.3. $\alpha\text{-}[\text{PVW}_{11}\text{O}_{40}]^{4-}$ (**3**)

Compound **3**, which possesses a higher reduction potential than **1** (0.80 V vs. NHE at pH 5 compared to an estimated 0.48 to 0.58 for the sodium salt of the $\alpha\text{-}[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ anion), is more effective at delignification [49]. Using **3** in an ME sequence at pH 1.5, pulp 1 was delignified to a kappa number of 7.6, while that for the parallel control was 18.9. After the reaction, 43.6% of the vanadium present had been reduced to V^{IV} . However, compound **3** is stable only at pH values below 2, at which considerable cellulose degradation occurs at elevated temperatures. In addition, its one-electron reduced form is known to react only very slowly with dioxygen [61].

5.2.4. $\alpha\text{-}[\text{SiVW}_{11}\text{O}_{40}]^{5-}$ (**4a**)

In an effort to show that losses in pulp quality observed in trials using **1** and **3** were due to hydrolysis alone, and that POM delignification could be both effective and highly selective, we sought a POM salt stable at neutral or higher pH values, which possessed a reduction potential close to, but below, that of dioxygen. The POM salt chosen was $\alpha\text{-K}_5[\text{SiVW}_{11}\text{O}_{40}]$ (**4a**), which is stable in water up to a pH of approximately 8, beyond which decomposition and precipitation of a light yellow material are observed. After reflux in pure water at pH 7, no changes were observed in the position or peak-width at half-height ($\nu_{1/2}$) of the ^{51}V NMR signals of **4a** or **4b** (after oxidation with Br_2)

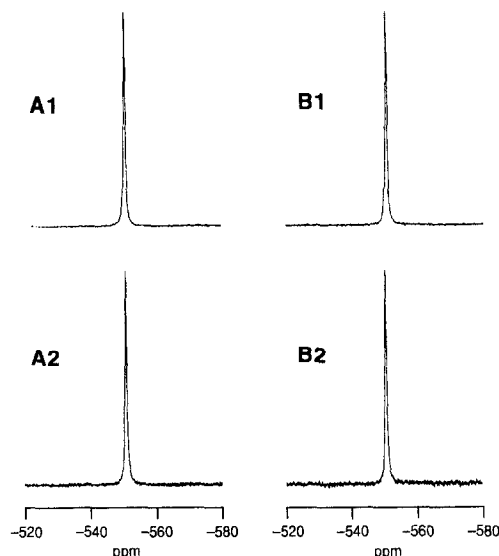
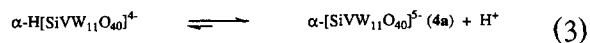


Fig. 7. ^{51}V NMR spectra of solutions of **4a** (before, A1 and after, B1) and **4b** (before, A2 and after, B2) 55 days at reflux in pure water at pH 7. Prior to acquisition of spectra, solutions of **4b** were oxidized to **4a** with Br_2 .

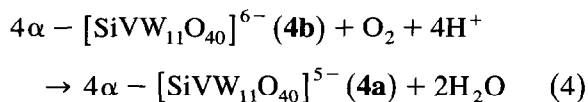
after 55 days (Fig. 7). Assuming an instrument sensitivity of 99% for the ^{51}V nucleus, this indicates a *minimum* half-life for each of 8.6 years and demonstrates that the reduction of **4a** to **4b** is entirely reversible. After 112 days, a broad signal of very low intensity (less than 1%) was observed in the solution of **4a** ($\tau_{1/2} = 21.2$ y) and no changes were observed in spectra of **4b** after 208 days ($\tau_{1/2} = 39.3$ y). However, when heated in phosphate buffer at pH 7, an equilibrium is established rapidly between **4a**, $[\text{P}_2\text{W}_5\text{O}_{23}]^{6-}$ and $[\text{SiV}_x\text{W}_{12-x}\text{O}_{40}]^{(4+x)-}$, $x = 2, 3$ (both identified by ^{31}P and ^{51}V NMR and by UV-vis spectroscopy), that is shifted towards the diphosphate and polyvanadates by relative increases in the concentration of phosphate buffer. During bleaching (0.20 M phosphate, 0.05 M **4a**), the concentration of **4a** remains at 90–95% of its initial value.

The potential of the **4a/4b** couple, E , has been measured at 0.64 V vs. NHE at pH 5 [49] and in a later report it was measured to be 0.72 V at pH 4.5 [62]. After dissolving **4a** in a pH 5 acetate buffer solution, we measured a reduction potential of $E = 0.69$ V (5.0 mM **4a**, 0.2 M

sodium acetate buffer, scan rate = 20 mV/s, $E_{pa} = 0.72$ V, $E_{pc} = 0.66$ V, $E_{pa} - E_{pc} = 60$ mV, $E = (E_{pc} + E_{pa})/2$). Remarkably for aqueous solutions of a transition-metal complex, the reduction potential of the α -[SiVW₁₁O₄₀]⁵⁻ anion remains nearly constant over a 1 000 000 fold change in hydrogen ion concentration, from pH 2 to 8 (Fig. 6). Thus, at pH 1.8 (a pH at which **4a** is unlikely to be stable), an irreversible potential of 0.68 V (as $E_{pc} + E_{pa})/2$) was measured (5.0 mM **4a**, 0.2 M, pH 7 potassium phosphate buffer to which a small amount of phosphoric acid was added immediately prior to the potential sweep experiment, scan rate = 20 mV/s, $E_{pa} = 0.74$ V, $E_{pc} = 0.62$ V, $E_{pa} - E_{pc} = 120$ mV). At pH 8.1, the high end of the stability range of **4a**, an irreversible potential of 0.64 V was measured (0.1 M sodium acetate, scan rate = 20 mV/s, $E_{pa} = 0.70$ V, $E_{pc} = 0.57$ V, $E_{pa} - E_{pc} = 130$ mV). These results suggest that the pK_a of the reaction shown in Eq. (3) is considerably less than 1.8 and that over the entire pH range studied, one-electron reduction of **4a** to **4b** is not accompanied by protonation.



Surprisingly, **4b** was not oxidized by dioxygen after 208 days at reflux at pH 7 (the condenser was open to the atmosphere over the course of the experiment). In addition, little oxidation was observed when pH 7 solutions of **4b** in phosphate buffer were heated to 150°C for 4 h under 100 psig of dioxygen. This despite electrochemical data indicating that the reaction (Eq. (4)) should be favored by 12.5 kcal/mol (taking E (**4a/4b**) as 0.68 V and the reduction of O₂ to water at pH 7 as 0.815 V) [55].



The rate limiting step in the reaction of **4b** could be the single-electron reduction of O₂ to the superoxide anion radical, O₂·⁻, which would have a ΔG^0 at pH 7 of +23.3 kcal/mol,

the reduction of O₂ to O₂·⁻ requiring an input of 0.33 V [56]. If this step were forced to occur via an outer sphere mechanism, a very low reaction rate would be expected. This might be the case if the V^{IV} ion in **4b** is coordinatively saturated by the pentadentate α -[SiW₁₁O₃₉]⁸⁻ ligand, if expansion of the vanadium coordination environment to include a seventh ligand does not occur and if the vanadyl complex α -[SiV(O)W₁₁O₃₉]⁶⁻ (**4b**) is not labile at neutral pH. In contrast, aqueous vanadyl ions (VO²⁺), which possess labile aqua ligands and range in oxidation potential from approximately 0.95 to 0.75 V over the pH range of 2 to 4, are oxidized by dioxygen at pH values greater than 2.5 [19]. After 1 week at 14°C, conversions of 0.01 M solutions of VO²⁺, sealed under air and shaken in stoppered bottles at *initial* pH values of 3.5 and 4.9, were 21% and 76%, respectively. Reaction rates were much enhanced by heating to 70°C [63]. At the same time, the reduced form of **6**, α -[SiMn^{II}(OH₂)W₁₁O₃₉]⁶⁻, which at pH 5 possesses an oxidation potential very close to that of **4b**, but which contains a labile water molecule on the sixth coordination site of the Mn^{II} ion [64], is also oxidized very slowly at elevated temperature under an O₂ pressure of several atmospheres.

Bleaching trials using **4a** were carried out anaerobically at pH 7 in phosphate buffer using pulp 1 (kappa number 33.6 and viscosity of 34.2 mPa s). Microkappa numbers and viscosity values for the average of three EM₁M₂M₃E bleaching sequences, a control sequence and two different CE bleaching reactions, obtained using two Cl₂ loadings are shown in Fig. 8. The POM bleaching sequence (Fig. 8, solid line) is as selective as the CE sequence down to a kappa number of 10 (7.4% Cl₂) and more selective at lower kappa numbers (9.0% Cl₂). 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 even at pH 7 some cellulose hydrolysis occurs under the conditions of the bleaching reaction. (In this regard, it

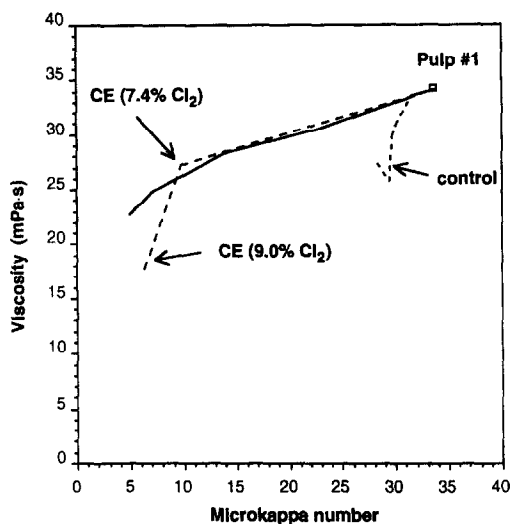


Fig. 8. Microkappa numbers and pulp viscosity values for the average of three $M_1M_2M_3E$ bleaching sequences performed using **4a** (solid line), for a POM-free control sequence and for two CE bleaching sequences (see text). The two CE runs, one performed using 7.4 wt% Cl_2 and the other using 9.0 wt% Cl_2 , are plotted together as a single curve.

should be noted that the pH values of the POM liquors dropped to near 6 during the M stages, while that of the control reaction remained at 7 throughout.)

A $M_1M_2M_3E$ sequence was performed on a larger scale to provide pulp for the determination of pulp yield and papermaking properties. As shown in Fig. 9, the kappa-viscosity curves of the POM trials fall slightly below those obtained using the (C/D)E sequence. In industry, substitution of chlorine dioxide (D) for elemental chlorine (C) is done to improve the selectivity of the delignification step and to decrease the amount of chloro-organic compounds produced per ton of pulp. Average yield of the POM delignified pulps was $89 \pm 3\%$, while that of the POM-free control was 89% and that of the C/D 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 drop in viscosity observed in each case. Even so, the POM delignified pulps possess papermaking

properties close to those of the C/D delignified sample. Papers made from the C/D delignified pulps possess slightly higher tensile indices, while those made from the POM pulps possess slightly higher tear indices.

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, the industry standard. For example, after modest attempts at optimization, pulp 2 was delignified by **4a** to a microkappa No. of 4.7 and a viscosity of 23.0 mPa s, after alkali extraction. In addition, the POM reactions described here were run at pH 7 (phosphate buffer). POM complexes stable at pH 9 are currently being studied and new ones developed. 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 groups present in residual lignin. Both trends are expected to facilitate further optimization of the POM delignification reactions and to allow for selective delignification down to very low kappa numbers.

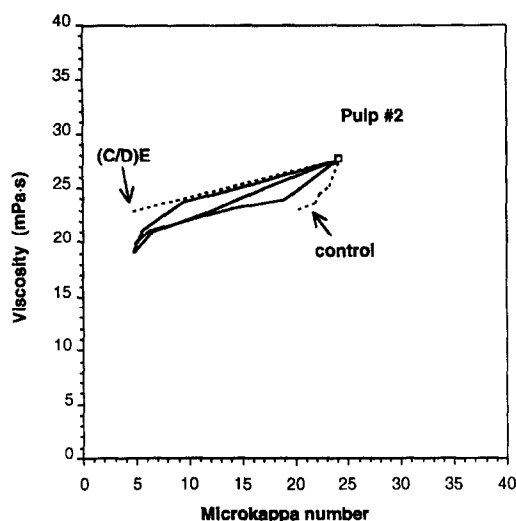


Fig. 9. Microkappa numbers and pulp viscosity values for three $M_1M_2M_3E$ sequences performed using **4a**, for a POM-free control sequence and for a single (C/D)E sequence (see text).

5.2.5. α -[BVW₁₁O₄₀]⁶⁻ (5)

In this regard, a 2.0 mM solution of the tungstoborate complex, α -[BVW₁₁O₄₀]⁶⁻ (5), in pure water at 80°C appeared stable up to pH values of approximately 9.5 upon addition of small aliquots of a 0.1 M solution of sodium hydroxide. At the same time, its reduction potential is substantially more negative than that of 4a (Fig. 6) and a bleaching trial was performed to determine whether effective delignification might still occur near the pK_a of the phenolic lignin substrate. The bleaching experiment (M₁) was carried out using conditions established for 4a (0.05 M 5, 125°C, etc.), except at an initial pH of 9.6 using carbonate buffer. Only modest delignification was observed (the kappa number after the M₁ stage was 19.7). However, because the pH of the solution dropped rapidly to pH 8.5, the effectiveness of 5, or more significantly, of POM complexes with reduction potentials near that of 5, at pH 9–10, has yet to be determined.

The carbonate-buffered bleach liquor was analyzed to determine whether the drop in pH reflected degradation of 5. The solution was reoxidized by addition of a slight excess of Br₂ prior to analysis by ⁵¹V and ¹¹B NMR (see experimental section). The oxidized solution had a pH of 8.4. Two sharp signals are observed in the ⁵¹V NMR spectrum of the same Br₂ oxidized bleaching solution (Fig. 10). The more intense signal at -16 ppm relative to HVO₄²⁻ (23 Hz, -576 ppm if referenced to VOCl₃), corresponds to intact 5 [65]. The narrow resonance at 50 ppm (51 Hz, -510 ppm relative to VOCl₃) contains 35% of the vanadium initially present in 5 and might tentatively be assigned to [V₂W₄O₁₉]⁴⁻ [66–69].

In order to gain further insights into the roles of vanadium oxidation state, pH and carbonate buffer [70] on the demetalation reaction, a low-dimensional matrix of control experiments (see experimental section) was performed and followed by ⁵¹V NMR.

The results are summarized as follows. After reflux at pH 8.5 in the absence of carbonate

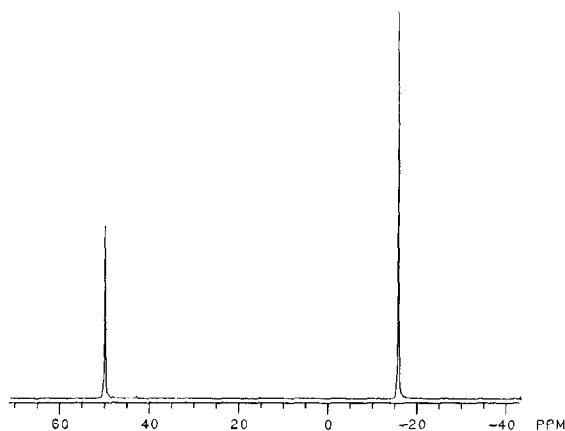


Fig. 10. ⁵¹V NMR spectrum of 5 after reaction with pulp in carbonate buffer (see text).

buffer, little if any demetalation of 5 is observed. However, under the same conditions, the one-electron reduced complex α -[BVW₁₁O₄₀]⁷⁻ is demetalated to a limited extent (ca. 10%). When carbonate buffer is present, some demetalation of 5 is observed after 18 h at room temperature (ca. 1%), while more is observed in the case of α -[BVW₁₁O₄₀]⁷⁻ (ca. 5%). These results suggest that the vanadyl ion (V^{IV}=O)²⁺ is more labile than the vanadate ion (V^V=O)³⁺.

5.2.6. α -[SiMn^{III}(OH₂)W₁₁O₃₉]⁵⁻ (6)

In addition to V^V, d-electron-containing transition-metal ions may also be used in bleaching. One candidate, attractive from both conceptual and pragmatic points of view, is manganese. Manganese peroxidase, one of the extracellular peroxidases excreted by some lignin degrading fungi, oxidizes Mn^{II}, abundant in the cell wall, to Mn^{III}. Turnover rates for this enzyme are dramatically accelerated by the presence of α -hydroxy acids, metabolites present in and around fungal hyphae, which are thought to chelate and stabilize Mn^{III} ions at or near the active site [71]. The α -hydroxy acids stabilize the Mn^{III} ions, which would otherwise disproportionate rapidly within the cell wall (pH 4) to dark insoluble MnO₂ and Mn^{II}. Instead, the chelated Mn^{III} cations are believed to penetrate the cell

wall where they are capable of oxidizing a range of phenolic lignin substructures.

Lignin peroxidases, in their porphyrinato[Fe^{IV}=O] cation radical (compound I) and neutral (compound II) forms are capable of oxidizing many alkyl and methoxyl substituted benzenes, such as those present in lignin, to cation radicals [72]. On the other hand, most of the pores within intact fiber walls, defined by loosely oriented 3–4 nm diameter cellulose microfibrils containing bulky pendant hemicellulose chains, seem too small for easy access by these enzymes. For instance, spherical dextrans 1.0 nm in diameter can penetrate 84% of the cell-wall volume accessible to water, while those 10 nm in diameter can penetrate only 14.4% of the water accessible domain [73]. (For comparison, Keggin anions are 1.1 nm in diameter and the sizes of POM anions of all types range from 0.9–3.0 nm.) Thus, the manganese peroxidase system could be used by the fungi to penetrate relatively intact cell walls.

Although bleaching systems have been developed using manganese peroxidases, delignification rates are too slow for commercial application [74]. Bleaching trials using α -[SiMn^{III}(OH₂)W₁₁O₃₉]⁵⁻ (**6**) were carried out to determine whether, when stabilized in aqueous solution by the α -[SiW₁₁O₃₉]⁸⁻ ligand, Mn^{III} could be used at elevated temperatures to obtain commercially relevant delignification rates. Another impetus for using manganese is its low cost and high environmental compatibility.

Results of a bleaching trial using **6** at pH 5 in acetate buffer are shown in Fig. 11. The overall kappa number/viscosity relationship is similar to that obtained using **4a** under the same conditions. This is not surprising considering that: (1) both **4a** and **6** are capable of oxidizing phenolic substrates, (2) the reduction potential of **6** at pH 5 (0.68 V vs. NHE) is close that of **4a** at the same pH (Fig. 6), and (3) model studies strongly suggest that only phenolic lignin substructures are substrates for **4a**. To our knowledge, no detailed mechanistic information is yet available regarding the electron-transfer mechanisms op-

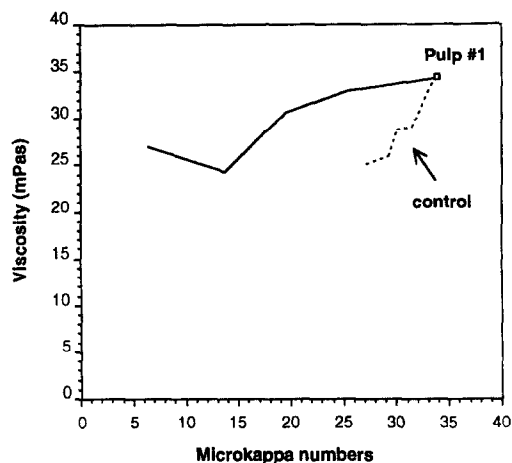


Fig. 11. Microkappa numbers and pulp viscosity values for a M₁M₂M₃E sequence performed using **6** and for a POM-free control sequence (see text).

erating in the reduction of **4a** or **6** by phenols or phenoxyl radicals in water.

The reduced form of **6**, α -[SiMn^{II}(OH₂)W₁₁O₃₉]⁶⁻ (**7**), is not reoxidized by oxygen at a rate suitable for commercial use. However, the tungstoborate analog, α -[BMn^{II}(OH₂)W₁₁O₃₉]⁷⁻, is reportedly easily oxidized [50]. This, and other Mn-containing POMs, such as α -[SiW₁₁O₃₉[Mn^{II}(OH₂)₃]¹⁰⁻ [75], and new ones under development in our laboratories, such as [AlMn^{III}(OH₂)W₁₁O₃₉]⁶⁻, and others prepared using hydrothermal methods (see below), are all promising candidates for use in bleaching.

5.3. Mechanism and kinetic analysis

Information concerning the kinetics of POM delignification of kraft pulps can aid in process optimization and design of commercial bleaching reactors. However, kraft pulp as a substrate is not well-defined, and so, the results of kinetic modeling cannot be used to directly determine reaction mechanisms. Over the last 20 years considerable progress has been made in defining the nature and frequency of chemical substructures present in the residual lignin component of wood fibers subjected to kraft pulping. Al-

though a comprehensive structural model does not yet exist, these efforts have provided information concerning the most abundant structures present [5,6]. For example, approximately 15% of the phenyl structures present in native softwood lignin are hydroxylated. This figure rises to ca. 20–40% for residual kraft lignin [6]. The phenolic end-groups arise from the cleavage of aryl ether linkages during kraft pulping. Based on model studies, these phenolic groups appear to be the primary substrates for **4a** in its reactions with kraft pulp.

Additionally, there are uncertainties associated with the macro-molecular structure of wood fibers. Models of woody tissue place the lignin within a carbohydrate matrix [1,2]. This matrix is dominated by cellulose microfibrils, 3–4 nm bundles of organized cellulose chains, with lignin polymer forming an extended three-dimensional network between the microfibrils. From the perspective of bleaching, the nature of this matrix is important because it can restrict the access of oxidant to the lignin substrate, and thus modify the apparent reaction kinetics. Thus, both the complex chemical nature of residual lignin and the heterogeneity and ill-defined phase boundaries of the lignocellulosic matrix, complicate the analysis of kinetic data.

In reactions of **4a** with both the non-phenolic and phenolic lignin dimer models I and II (Fig. 12), under actual delignification conditions (pH 7 phosphate buffer, 3 h at 125°C) no reaction is seen with I, while rapid reaction, leading to dimer cleavage, is observed with II [40]. Based

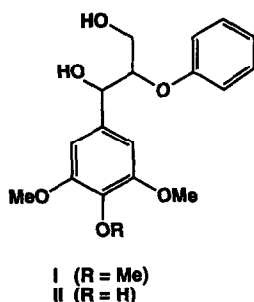


Fig. 12. Non-phenolic and phenolic β -aryl ether lignin substructure models.

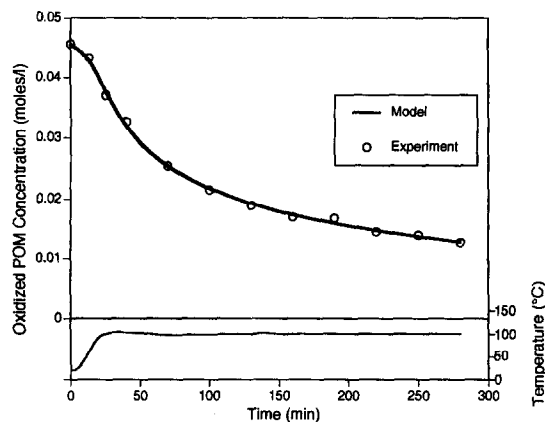


Fig. 13. Concentration of oxidized **4a** in the solution containing slurried pulp fiber as a function of time for a single batch bleaching reaction. The symbols are experimentally determined values and the line is that predicted using a kinetic model (see text). Reaction variables and conditions are as described in the experimental section and the temperature/time profile is inset below.

on consideration of the relative reactivities of the dominant chemical structures present in residual kraft lignin, these results strongly suggest that only hydroxylated phenyl substructures are substrates for **4a**. However, although the reaction of **4a** with lignin model II is very rapid, delignification by this POM requires several hours of treatment. This observation suggests that: (1) residual lignin contains a wide variety of phenolic structures, some of which react with **4a** more slowly than others and/or that (2) phenolic moieties are rapidly consumed and the continuous generation of new ones is rate limiting, and/or that (3) mass transport and other phenomena associated with the nature and structure of the partially lignified pulp fibers are limiting. These options are discussed in the context of the preliminary kinetic analysis presented below.

Data obtained in bleaching experiments done on kraft pulp 2 using **4a** are shown in Fig. 13 and Fig. 14 (see experimental section). Both figures indicate that oxidized POM is consumed as the bleaching progresses. The lignin contents, as microkappa numbers, of the pulps before and after each run were also determined. Data in

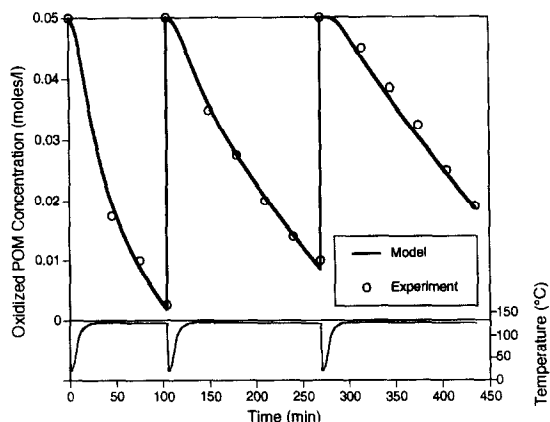


Fig. 14. Concentration of oxidized polyoxometalate in the solution containing slurried pulp fiber as a function of time for three successive batch bleaching reactions. The symbols are experimentally determined values and the lines are those predicted using a kinetic model (see text). Reaction variables and conditions are as described in the experimental section and the temperature/time profile is inset below.

Fig. 13 are from a bleaching run done at 100°C. The slow initial reaction rate corresponds to the time required to heat the reactor to temperature, usually about 45 min. Fig. 14 shows data obtained from three successive 125°C batch reactions. These data show two discontinuities that correspond to the replacement of the reduced POM solution with fresh, fully oxidized solution. At each of these points the pulp was removed from the cooled reactor, washed with water, and mixed with fresh POM solution. The reactor was then reheated to the operating temperature. This allowed the bleaching to be extended for more complete removal of lignin from the pulp and provided some insight into the likely behavior of the pulp in a multi-stage bleaching system.

The lines in the figures are model predictions calculated using kinetic parameters obtained from a simultaneous least squares fit of three data sets, which include data obtained at two different temperatures. Modeling was done by numerical integration of the assumed rate expressions using rate constants possessing Arrhenius temperature dependencies. Lignin concentrations in pulp slurries of known consistencies

were represented by kappa numbers. Rate expression parameters were optimized to minimize deviation between the experimental data and the kinetic model.

The data set was best described by the model shown in Eq. (5), Eq. (6) and Eq. (7), which consists of two independent parallel reactions: a fast reaction, first order in both oxidized POM concentration ($[POM_{ox}]$) and lignin concentration (designated $[L_f]$), and a slow, zeroth order reaction in which the rate was unaffected by either $[POM_{ox}]$ or lignin concentration, $[L_s]$. The two reactions can be seen in Fig. 14 where the part of the plot showing the progress of the initial bleaching step has curvature indicative of a dependence on $[POM_{ox}]$ while by the third bleaching step the progress is nearly linear with time, showing no such dependence. After assuming the functional dependence of the rate expression on $[POM_{ox}]$ and lignin concentration, one can then estimate the activation energies of these two reactions using a least squares error definition. The activation energies of the rate constants that minimize the errors for the whole data set are 3.7 ± 0.1 and 27.1 ± 0.04 kcal/mol for the second order and the zeroth order reactions respectively. The fraction of total lignin that reacts with second order kinetics, L_f , was also adjusted to give the lowest square deviation. The best value was $24 \pm 2\%$. The balance of the lignin, L_s , was assumed to react via the zeroth order kinetics. The uncertainties in the fitted parameters were defined as the change that results in a 10% increase in the sum of the error squares.

$$-\frac{d[POM_{ox}]}{dt} = k_f[POM_{ox}][L_f] + k_s \quad (5)$$

$$-\frac{d[L_f]}{dt} = k_f[POM_{ox}][L_f] \quad (6)$$

$$-\frac{d[L_s]}{dt} = k_s \quad (7)$$

Given the complex nature of the lignin substrate, conclusions from these experiments and

modeling are tenuous. The results do, however, provide some useful insights. The activation energy of the second-order reaction, 3.7 kcal/mol, is lower than the values typically observed for oxidation reactions. This suggests that the apparent rate of this reaction is likely controlled by a mass transport resistance. If this is the case, then the first-order dependence on $[POM_{ox}]$ might result from a linear dependence of mass transport rate on concentration. The other reaction, however, exhibits an activation energy near the value one would expect in a chemical-reaction-controlled process. At the same time, however, the reaction rate unexpectedly appears to be independent of both $[POM_{ox}]$ and $[L_s]$. One possible explanation of the zeroth order dependence of reaction rate on $[POM_{ox}]$ and $[L_s]$ is that there are a fixed number of phenolic reaction sites responsible for delignification and that these are saturated with oxidant at all times. Studies designed to better understand these and other observations are in progress. The import of the present analysis is that full understanding of the reactions of POMs within pulp fibers must include consideration of a number of issues arising from the effects of heterogeneity and surface phenomena.

5.4. Wet oxidation (unit operation D)

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 [76]. POM complex 1 was used to demonstrate the feasibility of wet oxidation because its reduced form reacts rapidly with oxygen. Initial studies using 1 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 neared

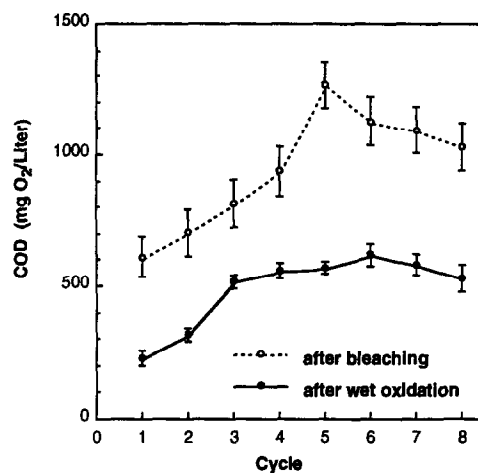


Fig. 15. Chemical oxygen demand (COD), in mg O₂/(l of compound 1 solution), determined for solutions leaving the anaerobic bleaching reactor (top curve) and for the same liquors after subsequent wet oxidation for 4 h at 150°C under 100 psig O₂ (bottom curve).

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 1 in eight successive bleaching/wet oxidation cycles. After several cycles, a steady state was achieved in the chemical oxygen demand (COD) values of the regenerated liquors leaving the wet oxidation reactor (Fig. 15, lower plot).

The amount of carbon dioxide generated during the wet oxidation reactions remained constant throughout all eight cycles of the experiment (Fig. 16). 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 proce-

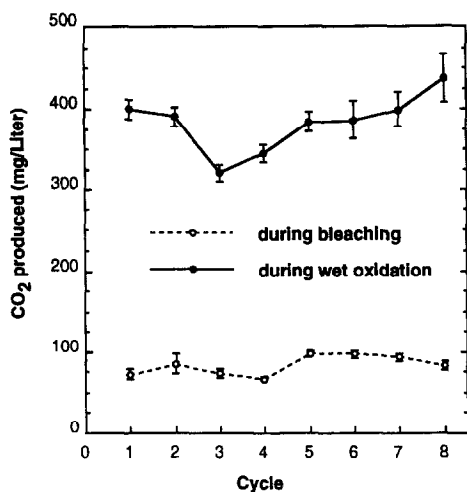


Fig. 16. CO₂ produced, in mg CO₂/(l of compound 1 solution), during anaerobic bleaching (bottom curve) and during subsequent wet oxidation for 4 h at 150°C under 100 psig O₂ (top curve).

ture (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 Fig. 15 and Fig. 16 demonstrate that mill closure could be achieved by using POM complexes to facilitate the wet oxidation of dissolved organic compounds. Additional work has shown that the extent of COD reduction during wet oxidation, a critical factor in achievement of a steady state, varies with the initial concentration and composition of the dissolved organics present in the spent bleach liquor. 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.

5.5. Design and development of new POM bleaching catalysts

Intrinsic to the technology outlined in this paper is a single species, a POM, that is required to fulfill multiple complex tasks. Chief among these tasks are the ability to selectively oxidize lignin versus cellulose in wood pulps and the ability to initiate autoxidation and other-

wise catalyze the complex oxidative mineralization (wet oxidation) of a spectrum of dissolved organic waste products from pulp bleaching. The goal of ongoing POM research is to optimize all the properties of these large complex molecules so that they can perform these tasks effectively and do so repeatedly without failure. Two key points then define the basis of POM catalyst design and development. The POM salts must, first, possess reduction potentials sufficiently positive for oxidizing phenolate anions in lignin and sufficiently negative to allow for spontaneous (energetically favorable) and kinetically facile reoxidation of the reduced POM salts by dioxygen, and second, be stable under the requisite operating conditions. Following from the discussions above, these operating conditions might include pH values of 9–10 to minimize cellulose hydrolysis, high temperatures to optimize the kinetics of wet oxidation, and resistance to degradation by species and conditions present during the four unit operations. Some of these potential POM degrading species include saccharide and lignin derived compounds that might demetallate the POM by chelation, the metal ions that occur in wood (particularly Mn and Fe ions), that might exchange with the POM metal ions, and precipitating agents of various kinds.

POM design and development will follow a conventional tack involving the targeting of a few compounds based on their redox potentials and other physical characteristics followed by attempted synthesis of these compounds. In other words, a guess, based on currently available data, of the best compounds will be made followed by serial synthesis, purification and finally evaluation. At the same time, another approach will be pursued that follows from our recent work seeking to correlate the genesis or self assembly of a catalyst with that catalyst's function [77]. This approach takes the concept of the pre-catalyst and catalyst generation in situ (production of the active specie(s) during operation or under catalytic conditions) and takes it some conceptual steps further. This approach

states that if the system is designed so that the catalyst forms not only from its components at the outset of the catalytic process but also during and at the end of the process, it will have a greater intrinsic stability with respect to the catalysis itself. Self assembly of a catalyst during the height of the reaction and at the end of the reaction implicates a stability of the catalyst with respect to damaging intermediates as well as inhibitors or poisons often present at the end of a catalytic process. If such comprehensive self assembly (spontaneous and kinetically facile catalyst formation from all catalyst components under all phases of the reaction) is demonstrated, a consequence is that some types of catalyst damage, specifically those involving catalyst degradation into its original synthetic components, will be effectively 'sensed' by the collective catalyst system and reversed [77]. In other words such degradation will be followed by catalyst reconstitution, the catalyst will effectively 'heal' itself.

Two related practical extensions of this approach deserve explication. First, the reaction conditions for the title technology should be used as the conditions of POM synthesis. The POMs that form under both the bleaching and wet oxidation conditions may well be more intrinsically stable (and may have a limited healing capability as described above) than those that do not. Such syntheses are underway including the use of hydrothermal conditions similar to those likely to be encountered during wet oxidation (Unit operation D, Fig. 5). Second, there should be more coordination intellectually and operationally between the companies that make catalysts and the companies that use them. Often one company makes the catalyst and has little or no interest in the detailed conditions under which the catalyst will be used and a second company uses the catalyst and pays little attention to the conditions under which the catalyst was made. Coordination of these efforts and fabrication of the catalyst(s) under the conditions of operation and processing should lead to better catalytic technology.

6. Concluding remarks

This article articulates a new approach, using complex multicomponent molecules, polyoxometalates (POMs), for the conversion of wood pulp into paper, an enterprise of major and long-standing import (economic and environmental) and current technological challenge. The approach is unique by intrinsic design and implementation in that the versatile capabilities of a single POM species are utilized to facilitate multiple operations that sum to the *selective* conversion of wood pulp to paper and non-toxic products (H_2O and CO_2) using air as the oxidant and water as the only solvent. While this approach currently promises to be highly 'green' as well as feasible energetically and otherwise, research will be required in a number of coordinated areas including a new approach to catalyst synthesis to bring optimal success to this effort.

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