

# Selective Transition-Metal Catalysis of Oxygen Delignification Using Water-Soluble Salts of Polyoxometalate (POM) Anions.

## Part I. Chemical Principles and Process Concepts

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### Keywords

Transition metal  
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Oxygen  
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### Summary

Polymeric metal-oxide anion complexes (polyoxometalates) may provide a means for using transition metals and oxygen (O<sub>2</sub>) to selectively delignify wood or wood pulp in effluent-free (closed) mills. The development of this chemistry, and associated process concepts, evolved from the observation that certain fungi use transition metals (Cu, Fe and Mn) to selectively transfer electrons from lignin to oxygen. Chemical, physicochemical and engineering issues pertaining to the development of aqueous transition-metal systems for selective delignification, and for mill closure, are outlined in this brief introduction to the title technology.

## Introduction

### *Transition-metal catalysis of oxidative delignification*

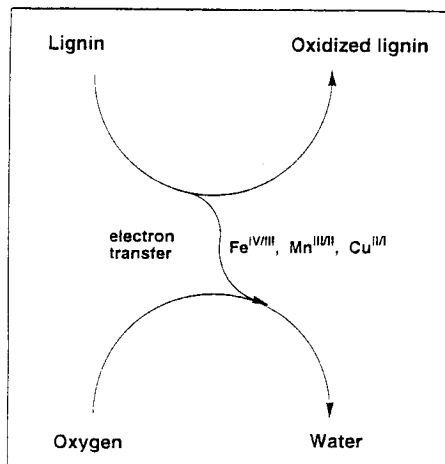
Oxygen, hydrogen peroxide and ozone are the most attractive alternatives to chlorine and chlorine dioxide with respect to both environmental impact and cost. Oxygen, while effective at depolymerizing and solubilizing lignin, is not sufficiently selective to fully delignify kraft pulps without extensive cellulose degradation (Gellerstedt *et al.* 1986). Unfortunately, significant improvement is limited by the fundamental reactivity of oxygen under autoxidation conditions. Alkaline hydrogen peroxide, while it reacts rapidly with chromophoric groups, is not effective at removing lignin (Gierer 1982). Better delignification is obtained using organic or inorganic peroxide derivatives such as per-formic or peracetic acids (Gierer 1982), dioxiranes (Pulliam 1993), persulfates (Springer and McSweeney 1986) or peroxometalates (Kempf 1983; Kubelka *et al.* 1992), each of which is more expensive than hydrogen peroxide itself. In addition, the use of peroxide compounds requires the removal or chelation of metal ions that might otherwise lead to rapid loss of active oxidant. Such metal-ion-catalyzed decomposition of peroxide is usually accompanied by the generation of unselective oxygen radicals, which damage pulp fibers (Gellerstedt

and Pettersson 1982). Ozone, while very effective at removing lignin, reacts rapidly enough with cellulose that high process selectivity is difficult to achieve on an industrial scale (Brolin *et al.* 1993).

A number of fungal enzyme systems capable of degrading lignin have been identified (Tien and Kirk 1983; Glenn and Gold 1985; Kirk and Shimada 1985; Glenn *et al.* 1986; Kirk *et al.* 1986; Kawai *et al.* 1987). These share two important characteristics: The terminal oxidant is molecular oxygen, and the transfer of electrons from lignin to molecular oxygen is mediated by transition-metal ions (Fig. 1). In addition, the final by-products of combined extra- and intracellular processes are water and carbon dioxide. These observations suggest that if properly controlled, transition-metal ions might be used to devise selective, oxygen-based, effluent-free delignification and bleaching technologies.

In general, however, the behavior and reactivity of transition-metal ions in water is difficult to control (Baes and Mesmer 1976). 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. In fungal lignin-degrading systems, these problems are avoided. The behavior and reactivity of the transition-metal ions used in electron transport are controlled by binding the metal ions within natural organic ligands, such as the protoheme active sites found in lignin and manganese

<sup>1</sup>) Brief descriptions of a *peroxometalate* process under development by Kemira Chemicals Oy (Helsinki) are reported in Chemical Marketing Reporter, July 4, 1994, p.5 and in Chemical Engineering, August 1994, p. 19.



**Fig. 1.** Schematic representation of transition-metal-mediated electron transfer from lignin to oxygen in the biological degradation of lignin by wood-rotting fungi.

peroxidases. With fungal peroxidases as a model, biomimetic bleaching systems have been devised using synthetic, water-soluble metalloporphyrin complexes (Labat and Meunier 1989; Skerker *et al.* 1990). Unfortunately, these metallo-organic complexes are difficult to prepare, require the use of expensive organic or inorganic peroxides and are inherently susceptible to oxidative degradation.

### Polyoxometalates

An alternative method for controlling the behavior and activity of transition-metal ions in water is to incorporate them into transition-metal oxygen-anion clusters, or polyoxometalate (POM) complexes (Pope 1983). Applications of POM complexes in oxidation catalysis have recently been reviewed (Pope and Müller 1991; Hill and Prosser-McCarthy 1995; Okuhara *et al.* 1996; Weinstock 1998).

#### Structure and physical properties

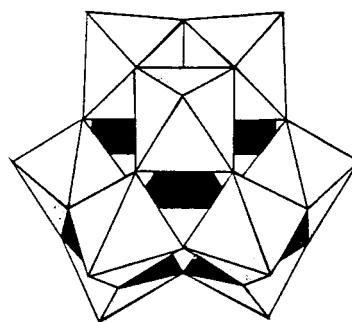
Polyoxometalates are a large, structurally diverse and rapidly growing class of inorganic clusters. They are composed of  $d^0$  metal cations  $\frac{1}{M}$  and in particular V(V), Mo(VI) and W(VI) in varying combinations  $\frac{1}{M}$  and oxide anions held together by metal-oxygen bonds (Pope 1983). The principal building blocks of POMs are  $MO_x$  ( $x = 4-6$ ) polyhedra (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, which contain only the  $d^0$  metal cations and oxide anions (general formula,  $M_xO_y^{n-}$ ), and the heteropolyanions, which contain one or more  $d$  or  $p$  block "heteroatom" cations,  $X^{n+}$ , in addition to the metal cations and oxide anions (general formula,  $XM_bO_c^{m-}$ ). 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 (Pope and Müller 1991). The most common and most thoroughly investigated class of heteropolyanions are the Keggin structures (Fig. 2). While POMs can range in size from  $9\text{Å}$

( $0.9\text{nm}$ ) to more than  $30\text{Å}$  ( $3\text{ nm}$ ), the Keggin structure has a diameter of ca.  $1.1\text{ nm}$ , similar to that of typical phenylpropane units in lignin. The negative charge of a POM can be counterbalanced by hydrophobic cations, such as  $Et_4N^+$  or  $Ph_4P^+$ , that render the complex soluble in organic solvents or by hydrophilic cations, such as  $Li^+$ ,  $Na^+$ ,  $K^+$  and  $NH_4^+$ , that render the complex soluble in  $H_2O$ .

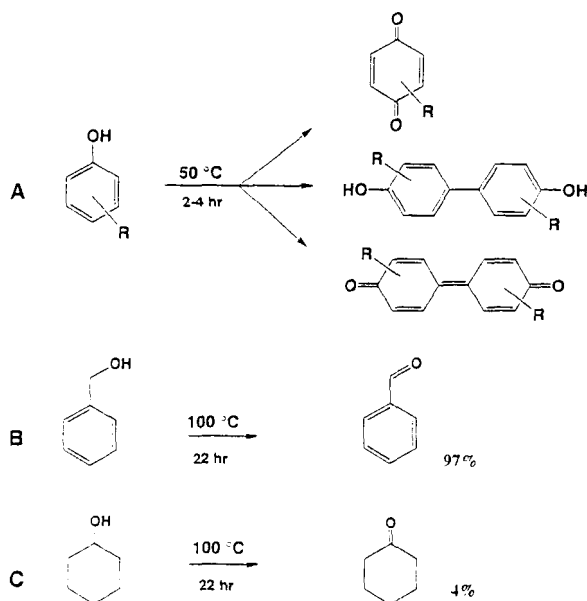
Several attributes make POMs attractive for the delignification of wood or wood pulp. First, POMs are readily prepared, often in a single step in  $H_2O$ , from inexpensive and minimally toxic compounds such as  $WO_4^{2-}$ ,  $MoO_4^{2-}$ ,  $PO_4^{3-}$  and  $SiO_3^{2-}$  (Pope 1983). Second, most of the key physical properties that control the fundamental reactivities of POMs (i. e., redox potentials, acidities, charges, solubilities, etc. ) can be controlled to a marked degree by choice of synthetic precursors and conditions. Third, POMs are inherently resistant to oxidative degradation (i.e., such  $d^0$  systems as glass, and many refractory ceramics are already in the maximum oxidation state achievable under conventional reaction conditions). Yet many families of POMs, including Keggin derivatives, can be reversibly reduced by one or more electrons (Weinstock 1998). In many cases, the reduced POM anions are readily oxidized by  $O_2$  (Weinstock 1998; Kozhevnikov 1998). Finally, one or more of the  $d^0$  metal ions in parent POM structures can be replaced by other  $d^0$  metal ions, such as V(V), or by  $d$ -electron-containing metal ions, such as Mn(III), Fe(III) or Co(III). Indeed, control over the chemically significant properties of POMs enumerated above vests, in part, in this rich substitution chemistry.

#### Reported reactions with lignin-like organic compounds

In 1992, Lissel and Kholdeeva independently reported that in organic solvents, the aerobic oxidation of alkyl-substituted phenols to monomeric 1,4-benzoquinones and to dimeric biphenols and diphenoquinones was catalyzed by vanadium-substituted POMs of the form  $[PV_nM_{12-n}O_{40}]^{(n+3)-}$  (A, Fig. 3). Earlier, Neumann (1991) reported that after 22 hrs at  $100^\circ\text{C}$  in toluene,  $[PV_2M_{10}O_{40}]^{5-}$  and oxygen cleanly converted benzyl alcohol to benzaldehyde (97%, 97 turn-overs) (B, Fig. 3) and 1-phenylethanol to acetophenone



**Fig. 2.** The  $\alpha$ -Keggin POM anion  $\alpha-[SiW_{12}O_{40}]^{4-}$  in polyhedral notation. The silicon heteroatom resides in a tetrahedral hole at the center of the structure (the  $SiO_4$  unit is shown in black). In polyhedral notation,  $MO_x$  units are depicted; the  $WO_6$  octahedra are shown in gray. Oxygen atoms reside at the vertices of the dark lines that define the  $MO_x$  polyhedra.



**Fig. 3.** Oxidations of **A.** alkyl-substituted phenols (Lissel *et al.* 1992; Kholdeeva *et al.* 1992), **B.** benzylic hydroxyls, and **C.** secondary aliphatic alcohols (Neumann *et al.* 1991), by  $\text{O}_2$  (1.0 atm) catalyzed by POM salts of the form  $\alpha\text{-}[\text{PV}_2\text{M}_2\text{O}_{10}\text{O}_{40}]^{5-}$  in acetic acid water in mixtures (**A**) and in toluene (**B** and **C**).

(94 % 94 turnovers). However, under the same conditions, very little cyclohexanol (3.6%) was oxidized to cyclohexanone (**C**, Fig. 3).

These results suggested that  $\alpha\text{-}[\text{PV}_2\text{M}_2\text{O}_{10}\text{O}_{40}]^{5-}$  and related POMs, such as  $\alpha\text{-}[\text{SiV}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{5-}$ ,  $\alpha\text{-}[\text{SiMn}^{\text{III}}\text{W}_{11}\text{O}_{39}]^{5-}$  and many others, might be highly selective for the oxidation of native or residual-kraft lignin. The ideal system would use oxygen more selectively than is currently possible and include a means for achieving mill closure (Weinstock and Hill 1994; Atalla *et al.* 1996; Weinstock and Hill 1996; Weinstock *et al.* 1996; Weinstock *et al.* 1997; Sonnen *et al.* 1997).

#### Oxidation by dioxygen

The POM anions useful in this context must be reversible oxidants, capable of undergoing repeated cycles of reduction and reoxidation without degradation. In addition, their oxidized forms,  $\text{POM}_{\text{ox}}$ , must have reduction potentials sufficiently positive to oxidatively degrade lignin, while at the same time sufficiently negative such that reoxidation with dioxygen is possible. In Figure 4 the reduction potentials of the POM anions  $\alpha\text{-}[\text{SiV}^{\text{V}}\text{W}_{11}\text{O}_{40}]^{5-}$  ( $\text{SiVW}$ ),  $\alpha\text{-}[\text{SiMn}^{\text{III}}\text{W}_{11}\text{O}_{39}]^{5-}$  ( $\text{SiMnW}$ ) and  $\alpha\text{-}[\text{PV}_2\text{Mo}_2\text{O}_{10}\text{O}_{40}]^{5-}$  ( $\text{PV}_2\text{Mo}$ ) are shown in relation to those for single- and four-electron reductions of dioxygen as a function of pH (Chanon *et al.* 1992; Weinstock *et al.* 1997). In general, all POM complexes (only three of many are included here) 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.

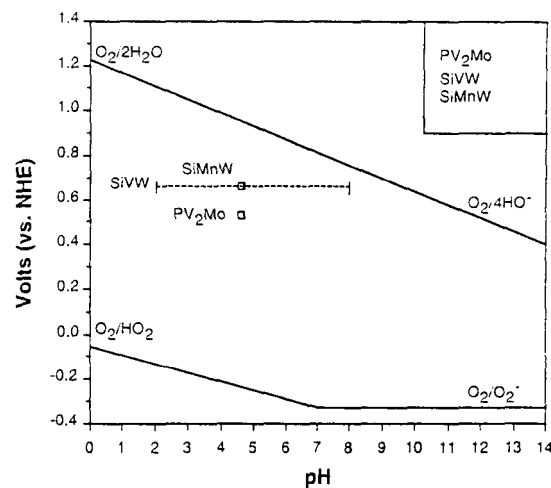
Selective, effluent-free delignification by POM salts and oxygen

#### Unit operations

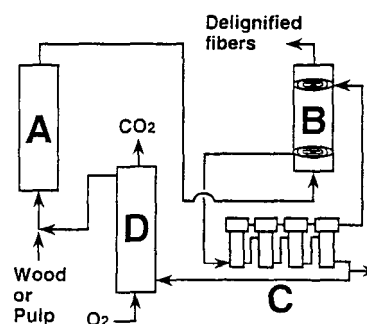
As currently envisioned, an oxygen-based, effluent-free POM delignification process will include four key unit operations: **A.** Bleaching, **B.** Pulp washing, **C.** Removal of wash water and undesired inorganic salts and **D.** POM-catalyzed wet oxidation of dissolved organic materials and simultaneous regeneration of the POM to its bleaching-active form (Fig. 5).

The two key chemical steps (unit operations **A** and **D**), which represent the selective conversion of lignin and oxygen to carbon dioxide and water, are summarized in Figure 6. In the first step (Fig. 5, unit operation **A**; Fig. 6, step 1), a slurry of unbleached pulp in an aqueous solution of fully oxidized POM salt ( $\text{POM}_{\text{ox}}$ ) is heated anaerobically. Here, the POM is converted to its reduced form ( $\text{POM}_{\text{red}}$ ) as it removes electrons from the residual lignin. By separating reoxidation of  $\text{POM}_{\text{red}}$  from anaerobic bleaching, exposure of the pulp to non-specific oxygen radicals is avoided entirely.

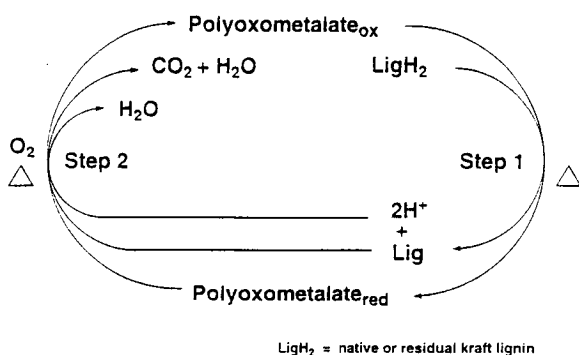
For example, under anaerobic conditions, aqueous solutions of  $\alpha\text{-}[\text{SiVW}_{11}\text{O}_{40}]^{5-}$  selectively delignify unbleached



**Fig. 4.** Reduction potentials of several  $\alpha$ -Keggin POM salts and of those for the one- and four-electron reductions of dioxygen, as a function of pH (see text).



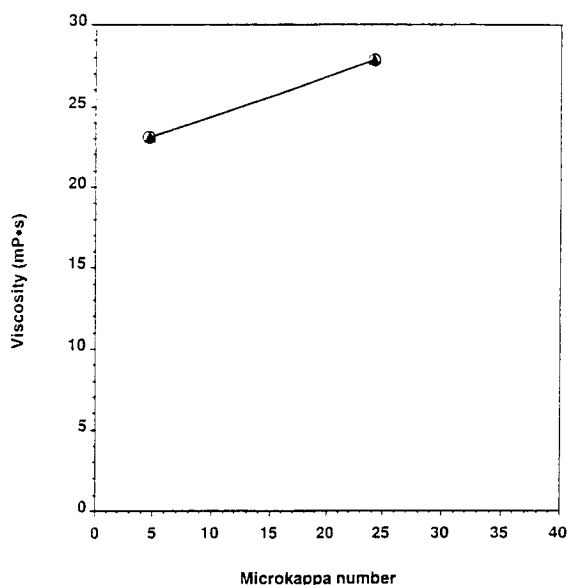
**Fig. 5.** Simplified schematic of an effluent-free POM delignification process (see text).



**Fig. 6.** Chemical steps in an effluent-free POM delignification process. Step 1: Anaerobic oxidation of lignin in wood or pulp fibers by fully oxidized POM complexes (POM<sub>ox</sub>); Step 2: Aerobic wet oxidation (mineralization) of dissolved organic compounds and regeneration of the reduced POM complexes (POM<sub>red</sub>) to their fully oxidized, delignification-active form.

softwood kraft pulps. After heating mixed-pine kraft pulp (kappa number 24.1, viscosity 27.8 mPa·s) at 3.0% consistency (csc) with  $\alpha$ -[SiVW<sub>11</sub>O<sub>40</sub>]<sup>5-</sup> (0.5 M in 0.5 M pH7 phosphate buffer) for 30 min at 125°C, kappa number and viscosity dropped to 8.1 and 25.1 mPa·s. After pulp washing and extraction with alkali (E), a kappa number of 4.7 and viscosity of 23.1 mPa·s were obtained (Fig. 7) (Weinstock *et al.* 1996). For comparison, the same pulp was delignified to the same extent using a chlorine/chlorine dioxide (C/D<sub>30</sub>)E sequence (Weinstock *et al.* 1995).

After leaving the bleaching reactor, the pulp is washed (Fig. 5, unit operation B). Preliminary washing studies indicate that unlike caustic, the POMs are not adsorbed onto pulp fibers (see Table 1). In experiments designed to



**Fig. 7.** Microkappa vs. viscosity for delignification of an unbleached mixed-pine kraft pulp (3.0% csc) by  $\alpha$ -[SiVW<sub>11</sub>O<sub>40</sub>]<sup>5-</sup> (0.5M, 0.5 hr at 125°C, followed by extraction with 1.0% alkali) in phosphate (0.35 M, pH 7) buffer solution (dark triangles) and by a (C/D<sub>30</sub>)E sequence (chlorine multiple = 0.19 with 30% dioxide substitution in the C/D stage) (open circles).

**Table 1.** Washing of POM salt from pulp after treatment with 0.05 M solutions of  $\alpha$ -Na<sub>6</sub>[Si<sup>IV</sup>W<sub>11</sub>O<sub>40</sub>]<sup>6-</sup> (POM<sub>red</sub> form) at 8% pulp consistency. Prior to the POM application, pulps were soaked overnight in 0.2 M pH 7 phosphate buffer and washed with water. Washing times indicate the time required for water (dilution factor of 3) to pass through the pulp mat (see text).

| POM treatment  | Washing time (min : sec) | Residual V (ppm <sup>a</sup> ) | Residual W (ppm <sup>a</sup> ) |
|----------------|--------------------------|--------------------------------|--------------------------------|
| 30 hrs at 25°C | 1:39                     | 3.57                           | 75.19                          |
| 1 hr at 125°C  | 0:47                     | 7.56                           | 170.4                          |

<sup>a</sup>Mass ratio of metal ion to oven-dried pulp.

simulate displacement washing systems, bleached hardwood pulps were pressed in a Büchner funnel after treatments with  $\alpha$ -[SiV<sup>IV</sup>W<sub>11</sub>O<sub>40</sub>]<sup>6-</sup> solutions. Each pulp sample was then washed with an amount of water corresponding to a dilution factor of three for the equivalent mass of pulp at 10% csc. The low levels of residual POM shown in Table 1 indicate that washing efficiencies of 99.9% and greater can be achieved relatively easily.

Wash water would then be recycled by evaporation using heat provided by low-grade steam. After concentration, a small spent liquor stream may be diverted so that non-process elements, such as mineral salts of Fe, Mn and Ca carried in with the pulp, can be purged (unit operation C). The concentrations of these elements may also be reduced by an acid-washing stage prior to delignification. A small portion of the POM stream may also be removed at unit operation C, or at an equally appropriate point, and re-refined at a rate dictated by its operational half-life.

After delignification, the bulk of the POM solution is passed directly to unit operation D. POM reoxidation and wet oxidation of dissolved organic compounds (Fig. 5). The much smaller POM stream derived from pulp washing, wash-water concentration, etc. (unit operations B and C), will also be sent to unit operation D. The POM stream entering this reactor contains oxidized lignin fragments as well as some polysaccharides, all of which enter the POM solution during delignification. To achieve mill closure, it is necessary to remove them. In addition, because delignification is carried out under anaerobic conditions, the POM in the stream entering unit operation D may be substantially reduced (POM<sub>red</sub>, Fig. 6). Before it can be used again in bleaching, POM<sub>red</sub> must be deoxidized. In unit operation D, POM<sub>red</sub> is deoxidized by oxygen under conditions that convert the dissolved lignin and polysaccharide fragments to carbon dioxide and water (Fig. 5, unit operation D; Fig. 6, step 2).

During delignification, a fraction of the  $\alpha$ -[SiVW<sub>11</sub>O<sub>40</sub>]<sup>5-</sup> present is converted to its one-electron reduced form,  $\alpha$ -[SiVW<sub>11</sub>O<sub>40</sub>]<sup>6-</sup> (POM<sub>red</sub>). The rate of reoxidation of the reduced anion by oxygen is slow, possibly limiting the usefulness of this system as a catalyst for wet oxidation (Fig. 6, step 2). Although a somewhat less potent delignification agent, the divandodecamolybdophosphate anion,  $\alpha$ -[PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub>]<sup>5-</sup>, is a very effective catalyst for wet oxidation. (Wood-pulp delignification can be achieved with

limited cellulose degradation when low concentrations of vanadomolybdophosphates are used in the presence of O<sub>2</sub> in water-organic solvent mixtures; Evtuguin and Pascoal Neto 1996, 1997; Evtuguin *et al.* 1997. )

In the presence of oxygen,  $\alpha$ -[PV<sub>2</sub>M<sub>0.10</sub>O<sub>40</sub>]<sup>5-</sup> acts as a catalyst and/or initiator of radical-chain autoxidation processes that result in the net conversion of all dissolved organic compounds to carbon dioxide and water (Duncan and Hill 1997). In a single (batch) reaction, complete conversion of organic compounds to carbon dioxide and water would be indicated by a decrease in the chemical oxygen demand (COD) of the substrate-containing solution to zero. The present process, however, is designed to operate in a continuous fashion. Here, the criterion for complete conversion of dissolved organics to carbon dioxide and water is the attainment of a constant (steady-state) COD value after repeated cycles of bleaching and wet oxidation.

Experiments utilizing single solutions of  $\alpha$ -[PV<sub>2</sub>M<sub>0.10</sub>O<sub>40</sub>]<sup>5-</sup> were carried out to demonstrate the feasibility of achieving a steady-state COD condition. After several cycles of bleaching followed by wet oxidation (4 hrs at 150°C and 0.7MPa of O<sub>2</sub>), steady-state COD values were observed in the POM liquors leaving the wet oxidation reactor (Weinstock *et al.* 1996; Weinstock *et al.* 1997; Sonnen *et al.* 1997). The amount of carbon dioxide generated during the wet oxidation reactions also reached a steady-state value after two cycles. These results demonstrated that mill closure could be achieved by using POM complexes to facilitate the wet oxidation of dissolved lignin and polysaccharide fragments.

#### pH control

During anaerobic delignification (Fig. 6, step 1), protons are liberated as lignin is oxidized and POM<sub>ox</sub> is reduced. The quantity of hydrogen ions produced corresponds to the extent of reduction of the POM anions (i. e., [POM<sub>red</sub>]). During the reoxidation of POM<sub>red</sub> in unit operation D (Fig. 6, step 2), these protons are consumed in the reduction of dioxygen to water. Thus, after a full cycle of delignification and wet oxidation, no net change in the hydrogen ion concentration, [H<sup>+</sup>], of the POM liquor occurs. However, to prevent large increases in [H<sup>+</sup>] during delignification, and consequent acid-catalyzed hydrolysis of the  $\beta$ -D-glucopyranoside linkages in cellulose, a pH buffer is needed. Because only an oxidatively inert buffer can withstand the conditions present in the wet oxidation reactor, organic buffers are unacceptable; however, inorganic buffers, such as sodium hydrogen phosphate, are good candidates.

The vanadoundecatungstosilicate anions used in the delignification experiment described above ( $\alpha$ -[SiVW<sub>11</sub>O<sub>40</sub>]<sup>5-</sup> and  $\alpha$ -[SiVW<sub>11</sub>O<sub>40</sub>]<sup>6-</sup>, Fig. 7) are stable in water at pH values from 3 to 8. For example, at 100°C their minimum half-lives in water at near-neutral pH are 21.2 and 39.3 years, respectively (Weinstock *et al.* 1997). However, when heated to 125°C in phosphate buffer, a stable equilibrium is rapidly established between  $\alpha$ -[SiVW<sub>11</sub>O<sub>40</sub>]<sup>5-</sup> and small amounts of additional POM complexes: [P<sub>2</sub>W<sub>5</sub>O<sub>23</sub>]<sup>6-</sup> and

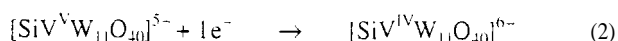
[SiV<sub>x</sub>W<sub>12-x</sub>O<sub>40</sub>]<sup>(4+x)-</sup>, x = 2, 3. Other oxidatively inert buffer systems have recently been developed for use with tungsten-based POM salts at near-neutral or higher pH values.

#### Comparison with oxygen delignification

As an oxygen-based process, POM delignification must be compared to the direct application of oxygen under alkaline conditions. Dioxygen (O<sub>2</sub>), as used in alkaline solution (eq. (1)), possesses a reduction potential of E° = -0.33 V vs. NHE (Fig. 4).



This is a much lower potential than that of  $\alpha$ -[SiVW<sub>11</sub>O<sub>40</sub>]<sup>5-</sup> (eq. (2)), which is 0.69V at pH values between 2–8 (Fig. 4).



Nevertheless, dioxygen is much less selective: When dioxygen is applied to pulp, a number of reduced oxygen species are formed via radical-chain autoxidation processes (Hill and Weinstock 1997). These include superoxide radical anions (OO<sup>•</sup>), peroxide anions (HOO<sup>•</sup>), hydroxyl radicals [HO] and the analogous alkyl derivatives, ROO<sup>•</sup>, ROO<sup>•</sup> and RO<sup>•</sup>. Some of these, such as HO, react rapidly with cellulose and show very little selectivity for lignin. Other autoxidation products, such as HOO<sup>•</sup>, react rapidly with quinonoid compounds and  $\alpha$ -ketones. Thus, when oxygen is used, a variety of oxidants, both selective and unselective, are formed. In contrast, when  $\alpha$ -[SiVW<sub>11</sub>O<sub>40</sub>]<sup>5-</sup> is used under anaerobic conditions, it is the only oxidant present throughout delignification. (An arguable exception is that certain intermediate products of ligin oxidation, such as quinonoid compounds, are themselves oxidants.) Radical-chain autoxidation processes do not occur, and higher selectivity to lower kappa numbers is achieved.

Later, however, during the aerobic regeneration of POM<sub>red</sub> (Fig. 5, unit operation D; Fig. 6, step 2), the tendency of oxygen to accept electrons and to form a variety of highly reactive species is used to full advantage. Here, many POMs (such as  $\alpha$ -[PV<sub>2</sub>LMo<sub>10</sub>O<sub>40</sub>]<sup>5-</sup>) can facilitate mill closure by catalyzing and initiating a variety of processes, including radical-chain autoxidation reactions, that degrade dissolved lignin fragments to CO<sub>2</sub> and water.

#### Conclusions

There are a minimum of six criteria that must be met by a single chemical system in order to realize the potential of POMs in the present context: (a) The POM must have a reduction potential sufficiently positive to oxidize lignin effectively (unit operation A); (b) the POM must be capable of facile reoxidation by oxygen under autoxidation conditions (unit operation D); (c) the system must be buffered to avoid drops in pH during bleaching; (d) the POM must not react irreversibly with the buffer components; (e) The system must be stable under operating conditions of pH and

temperature: and (f) the POM and buffer must be readily washed from pulp fibers.

To date, these criteria have been met and key unit operations demonstrated, using two different POM anions:  $\alpha$ -[SiVW<sub>10</sub>O<sub>40</sub>]<sup>5-</sup> and  $\alpha$ -[PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub>]<sup>5-</sup>. The results of laboratory trials of newly developed POM systems that possess the physical and chemical properties necessary to meet all the above-stated criteria will be reported shortly.

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