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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Summary
Polymeric metal-oxide anion complexes (polyoxometalates) may provide a means for using transition metals and oxygen (O₂) 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 McSweeny 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.
peroxides. With fungal peroxidases as a model, bio-
imetic bleaching systems have been devised using syn-
thetic, 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 poly-
oxometalate (POM) complexes (Pope 1983). Applications
of POM complexes in oxidation catalysis have recently
been reviewed (Pope and Müller 1991; Hill and Prosser-

Structure and physical properties

Polyoxometalates are large, structurally diverse and rapidly
growing class of inorganic clusters. They are composed of
d metal cations \( \frac{1}{n} \) and in particular V(V), Mo(VI) and
W(VI) in varying combinations \( \frac{1}{n} \) 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\(_x\) 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 metal cations and oxide anions (general formula, M\(_x\)O\(_y\)),
and the heteropolyanions, which contain one or more d or p
block “heteroatom” cations, X\(^\pm\), in addition to the metal
cations and oxide anions (general formula, X\(_m\)M\(_x\)O\(_y\)).
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 in-
vestigated class of heteropolyanions are the Keggin struc-
tures (Fig. 2). While POMs can range in size from 9Å
(0.9nm) to more than 30Å (3 nm), the Keggin structure has
a diameter of ca. 1.1 nm, similar to that of typical phenylpro-
pane units in lignin. The negative charge of a POM can be
counterbalanced by hydrophobic cations, such as Et\(_2\)N or
Ph, 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\(_2\)O.

Several attributes make POMs attractive for the delig-
nification of wood or wood pulp. First, POMs are readily
prepared, often in a single step in H\(_2\)O, from inexpensive
and minimally toxic compounds such as WO\(_4\)^{2-}, MoO\(_4\)^{2-},
P\(_2\)O\(_5\), and SiO\(_2\)^{2-} (Pope 1983). Second, most of the key
physical properties that control the fundamental reac-
tivities 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 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 metal ions in parent POM
structures can be replaced by other d 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\(_n\) Mo\(_{12-n}\) O\(_{40}\)]\(^{n+3}\) (A,
Fig. 3). Earlier, Neumann (1991) reported that after 22 hrs
at 100°C in toluene, [PV\(_2\) Mo\(_{10}\) O\(_{40}\)]
converted benzyl alcohol to benzaldehyde (97%, 97 turn-
overs) (B, Fig. 3) and 1-phenylethanol to acetophenone

![Fig. 1. Schematic representation of transition-metal-mediated electron transfer from lignin to oxygen in the biological degrada-
tion of lignin by wood-rotting fungi.](image1)

![Fig. 2. The \( \alpha \)-Keggin POM anion \( \alpha \cdot[\text{SiW}_{12}\text{O}_{40}]^\alpha \) 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\(_4\) octahedra are shown in gray. Oxygen atoms reside at the vertices of the dark lines that define the MO\(_x\),polyhedra.](image2)
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 (POMox) is heated anaerobically. Here, the POM is converted to its reduced form (POMred) as it removes electrons from the residual lignin. By separating reoxidation of POMred from anaerobic bleaching, exposure of the pulp to non-specific oxygen radicals is avoided entirely.

For example, under anaerobic conditions, aqueous solutions of α-[SiVW11O40]5- selectively delignify unbleached...
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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$_{ox}$); Step 2: Aerobic wet oxidation (mineralization) of dissolved organic compounds and regeneration of the reduced POM complexes (POM$_{red}$) 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$_{11}$O$_{40}$]$^5^-$ (0.5 M in 0.5 M pH 7 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 30 )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 simulate displacement washing systems, bleached hardwood pulps were pressed in a Büchner funnel after treatments with $\alpha$-[SiVW$_{11}$O$_{40}$]$^5^-$ 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$_{red}$, Fig. 6). Before it can be used again in bleaching, POM$_{red}$ must be deoxidized. In unit operation D, POM$_{red}$ 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$_{11}$O$_{40}$]$^-$ present is converted to its one-electron reduced form, $\alpha$-[SiVW$_{11}$O$_{40}$]$^-$ (POM$_{red}$). 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$_2$Mo$_{10}$O$_{40}$]$^-$, is a very effective catalyst for wet oxidation. (Wood-pulp delignification can be achieved with

<table>
<thead>
<tr>
<th>POM treatment</th>
<th>Washing time (min : sec)</th>
<th>Residual V (ppm)</th>
<th>Residual W (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 hrs at 25°C</td>
<td>1:39</td>
<td>3.57</td>
<td>75.19</td>
</tr>
<tr>
<td>1 hr at 125°C</td>
<td>0:47</td>
<td>7.56</td>
<td>170.4</td>
</tr>
</tbody>
</table>

Mass ratio of metal ion to oven-dried pulp.

Table 1. Washing of POM salt from pulp after treatment with 0.05 M solutions of $\alpha$-[SiV$_6$W$_{11}$O$_{40}$]$^-$ (POM$_{form}$) 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).

Fig. 7. Microkappa vs. viscosity for delignification of an unbleached mixed-pine kraft pulp (3.0% csc) by $\alpha$-[SiVW$_{11}$O$_{40}$]$^-$ (0.50 M, 0.19 with 30% dioxide substitution in the C/D stage) (open circles).
limited cellulose degradation when low concentrations of vanadium-molybdophosphates are used in the presence of O$_2$ in water-organic solvent mixtures; Evtuguin and Pascoal Neto 1996, 1997; Evtuguin et al. 1997.)

In the presence of oxygen, $\alpha$-[PV$_{1}$M$_{0}$O$_{40}$$]^{\cdot}$ 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$_{1}$M$_{0}$O$_{40}$$]^{\cdot}$ 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$_2$), 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$_{5-}$ is reduced. The quantity of hydrogen ions produced corresponds to the extent of reduction of the POM anions (e.g., POM$_{5-}$). During the reoxidation of POM$_{5-}$ 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$^+$], of the POM liquor occurs. However, to prevent large increases in [H$^+$] 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 vanadonudecatungstosilicate anions used in the delignification experiment described above ($\alpha$-[SiV$_{11}W_{12}$O$_{40}$$]^{\cdot}$ and $\alpha$-[SiV$_{12}$W$_{11}$O$_{40}$$]^{\cdot}$; 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 $\alpha$-[SiV$_{11}W_{12}$O$_{40}$$]^{\cdot}$ and small amounts of additional POM complexes: [P$_1$W$_2$O$_{40}$$]^{\cdot}$ and [SiV$_{11}$W$_{12}$O$_{40}$$]^{\cdot}$, $\alpha$=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$_2$), as used in alkaline solution (eq. (1)), possesses a reduction potential of $E^\circ$ = −0.33 V vs. NHE (Fig. 4).

$$\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^{\cdot-} \quad (1)$$

This is a much lower potential than that of $\alpha$-[SiV$_{11}$W$_{12}$O$_{40}$$]^{\cdot}$ (eq. [2]), which is 0.69V at pH values between 2–8 (Fig. 4).

$$[\text{SiV}_x\text{W}_{12-x}\text{O}_{40}$$]$_{5-}$ + 1$\text{e}^-$ → $[\text{SiV}_{11}\text{W}_{12}\text{O}_{40}$$]_{5-}^{\cdot}$ (2)

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 (0O$^-$), peroxide anions (HOO$^-$), hydroxyl radicals (HO) and the analogous alkyl derivatives, ROO$^-$, ROO$^-$ and RO. Some of these, such as HO, react rapidly with cellulose and show very little selectivity for lignin. Other autoxidation products, such as HOO$^-$, 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 $\alpha$-[SiV$_{11}$W$_{12}$O$_{40}$$]^{\cdot}$ is used under anaerobic conditions, it is the only oxidant present throughout delignification. (An arguable exception is that certain intermediate products of lignin 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$_{5-}$ (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$_{11}$M$_{0}$O$_{40}$$]^{\cdot}$) can facilitate mill closure by catalyzing and initiating a variety of processes, including radical-chain autoxidation processes, that degrade dissolved lignin fragments to CO$_2$ 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-\[\text{SiVW}_{11} \text{O}_{40}\]^{-5} \) and \( \alpha-\[\text{PV}_{2} \text{Mo}_{10} \text{O}_{40}\]^{-5} \). 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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