

A new environmentally benign technology and approach to bleaching kraft pulp. Polyoxometalates for selective delignification and waste mineralization

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Received May 10, 1995, accepted May 24, 1995.

Abstract. - A new technology based on polyoxometalates for bleaching and processing wood pulp in conjunction with paper manufacture is presented. In four Unit Operations not only is kraft pulp selectively delignified by polyoxometalates in an anaerobic process, but also all organic waste from the bleaching step is mineralized to CO₂ and H₂O by polyoxometalates in a complex aerobic process. The sum of the Unit Operations is the selective conversion of kraft pulp into a bleached pulp with attractive papermaking profiles (strength indices, mechanical properties, etc.), plus CO₂ and H₂O. Studies using dimeric lignin models link lignin fragmentation during anaerobic polyoxometalate delignification to a combination of oxidative and hydrolytic steps.

Introduction

The selective bleaching of wood pulp in conjunction with paper manufacture, one of the largest industries worldwide, has long been associated with significant environmental impact. Wood consists principally of two biopolymers: Cellulose, a structural polysaccharide that gives it tensile strength, and Lignin, a cross-linked, hydroxylated and methoxylated aromatic material that gives it color, resistance to biological attack, and structural rigidity^{1,2}. A principal goal in conversion of wood to high quality paper products is to selectively remove the lignin without damage to the cellulose. These paper products are manufactured using bleached pulps that are nearly all cellulose. Only minute quantities of residual materials derived from lignin during the pulping and bleaching processes remain in the paper. The industry, in most of the developed countries, has moved away from traditional Cl₂ based delignification processes because of the potential environmental impact

of chlorocarbon by-products^{3,4}. While many alternatives to Cl₂ have been developed in recent years, few oxidative bleaching agents for wood pulp match it in effectiveness and economy⁵.

O₂ and H₂O₂ are the most attractive alternatives to Cl₂ based technology both with respect to environment and economy⁶. We report here the design and preliminary development of a new approach to the selective bleaching (oxidative delignification) of wood pulp based on O₂ in combination with a remarkably versatile class of compounds called early transition metal oxygen anion clusters, or polyoxometalates (POMs for short). The new approach has the advantage of incorporating the concept of bleach mill closure, one of the long-term goals adopted by some in the industry.

POMs are a large and growing class of inorganic compounds composed primarily of the early transition metal cations in their *d*⁰ oxidation states (most commonly W^{VI}, Mo^{VI}, and V^V) and oxide anions that come in a variety of structures and sizes (6 to over 40 transition

metal ions)⁷⁻⁹. Many structural families of POMs, including the two shown in Figure 1, have an extensive and reversible redox chemistry. The versatility of POMs derives in part from the fact that their size, shape, negative charge density, redox potentials, transition metal compositions, and other molecular characteristics of direct pertinence to the catalysis of redox processes can be altered by synthetic routes that are becoming increasingly systematic. Several new processes based on the use of POMs either as acid or oxidation catalysts have been developed in recent years¹⁰⁻¹³ and the use of POMs as catalysts in homogeneous processes has just been reviewed⁹. Important historical precedents for the efforts elaborated here involve the first demonstration over two decades ago by the Novosibirsk group that some reduced polyoxometalates could be reversibly deoxidized by O₂¹⁴⁻¹⁶, the use of *d*-electron transition metal-substituted polyoxometalates as biomimetic oxidatively resistant analogs of metalloporphyrins for the catalysis of oxo transfer nine years ago by Hill and Brown¹⁷, and the use of thermodynamically optimized POMs of more than one *d*⁰ transition metal ion, referred to as "mixed addenda" POMs, as co-catalysts for the Pd-based oxidation of alkenes by Grate, Pettersson and co-workers¹⁸⁻²⁰.

The research on the title technology has been based at the U.S. Department of Agriculture Forest Service, Forest Products Laboratory (FPL), and involves investigators there, at Emory University (EU), at the University of Wisconsin Department of Chemical Engineering (UW) and the participation of a consortium of pulp and paper companies. The efforts at Emory have been and will continue to be directed primarily toward catalyst development, those at UW toward the reactor engineering, and those at FPL toward both areas. FPL also has and will continue to provide the principal

coordination with industry and conduct the evaluation of the wood products themselves.

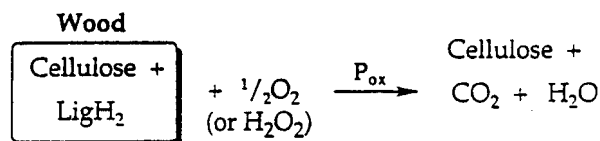
Results and discussion

Overview

The net process in the title technology is shown at the top of Figure 2, and the schematic diagram with four Unit Operations that constitute the net process is depicted in Figure 3. This new approach is environmentally benign in four ways: first, it doesn't use any chlorine-based compounds thus obviating the production of chlorocarbons; second, it uses only O₂ as the terminal oxidant, which is reduced to H₂O; third, it uses no organic solvents (only H₂O); and fourth, all the organic by-products derived from oxidative bleaching of the lignin are converted to CO₂ and H₂O. Significantly, the last point enables the entire process to be totally pollution free. This technology, if successful, will achieve the long sought goal of an effluent free mill (mill closure).

In Unit Operation A (bleaching), the wood pulp is heated under anaerobic conditions with an aqueous solution of the oxidized form of the polyoxometalate, P_{ox}, resulting

Net reaction



LigH₂ = native or residual kraft lignin

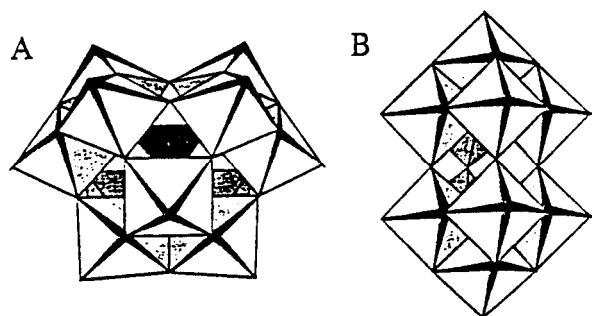


Figure 1. - Representative structures of polyoxometalates (POMs) in polyhedral notation. A: [PW₁₂O₄₀]³⁻ (a heteropolyanion); B: [W₁₀O₃₂]⁴⁻ (an isopolyanion). In polyhedral notation: the vertices are the nuclei of the oxide ions; the metal ions are inside each coordination polyhedron (WO₆ octahedron in this case).

Mechanism (General)

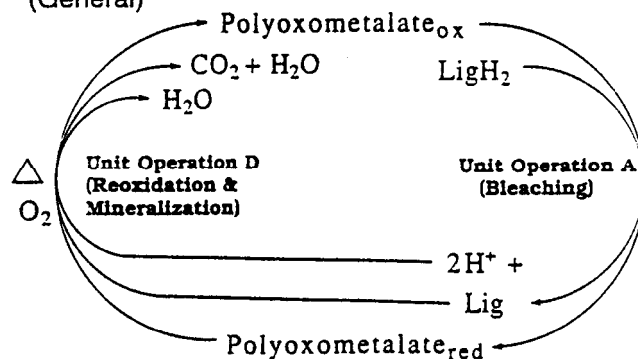


Figure 2. - TOP: the net process in the title technology. BOTTOM: the two chemical steps that add to the net process (Unit Operations A and D: see text).

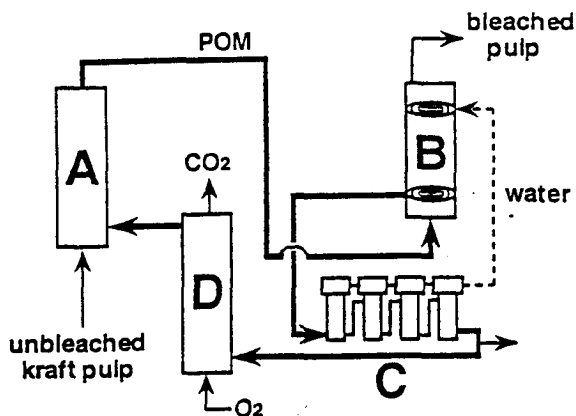
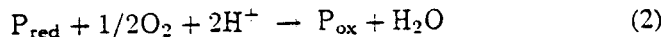
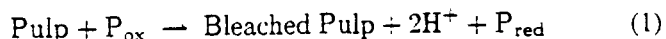


Figure 3. – Reactor and process diagram for the pollution-free bleaching and processing of kraft pulp. The 4 Unit Operations are described in the text.

in bleached wood pulp and reduced polyoxometalate, P_{red} , eq. 1. In Unit Operation B, the P_{red} and the partially oxidized lignin fragments, “Lig” in Figure 2, are removed from the largely undamaged cellulose by filtration and washing. In Unit Operation C, the wash water is concentrated and any undesirable inorganic salts are removed. Finally, in Unit Operation D, the P_{red} and dissolved organic materials from Unit Operation A are treated at higher temperature and under O_2 pressure. The P_{red} is deoxidized to P_{ox} , eq. 2, and the dissolved organic compounds are converted completely to CO_2 and H_2O . This later process is generally referred to as mineralization by chemists, wet oxidation by chemical engineers, and liquid combustion by other investigators. We now turn to the two chemical processes. Unit



Operations A and D, that sum to the net process (top of Figure 2).

Pulp bleaching (Unit Operation A)

The principal focus of bleaching reactivity is to selectively oxidize lignin: that is, to maximize oxidative degradation of the lignin and to minimize oxidation of the cellulose. For this selectivity, two criteria are dominant, operation at high pH, because cellulose is far more prone to undergo acid catalyzed depolymerization than is lignin, and low POM redox potentials. Cellulose is not just harder to oxidize kinetically but also substantially harder to oxidize thermodynamically. As a consequence, an oxidant, including an oxidized POM, P_{ox} , with

a potential in the window between the potentials of cellulose and lignin would be an attractive candidate. As minimal exothermicity generally correlates with higher selectivity, the ideal POM for bleaching would have a potential as close to that minimally required for eq. 1 to proceed at a satisfactory rate. At the same time this POM would require a potential sufficiently negative that reoxidation by O_2 , eq. 2, would be facile under the requisite operating conditions. The additional obvious feature of bleaching, eq. 1, is that maximal selectivity is likely to be achieved under anaerobic conditions as these preclude minimally selective and controllable O_2 -based radical chain (autoxidation) processes²¹.

The initial focus of the research has been on Keggin derivatives as this structural class (Fig. 1A) is the most extensive, the best studied, and the most modifiable of the POMs^{7,8}. Two Keggin derivatives with pH ranges of stability and redox potentials in or close to the targeted values were evaluated, $K_5[SiVW_{11}O_{40}]$, henceforth **1**²², and $\alpha\text{-Na}_x\text{H}_5\text{-}_x[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]$, henceforth **2**²³. The pulps of initial focus were unbleached mixed-pine kraft pulps. Figure 4 illustrates the results for bleaching of representative kraft pulps, **A**: by **1** (average of three bleaching trials) and by chlorine (traditional method at two different concentrations under standard industrial conditions); **B**: by **1** (three trials plotted individually) and by a mixture of Cl_2 and ClO_2 , formulated to duplicate the current state-of-the-art in chlorine-based delignification. Kappa number, determined by observing the reduction of permanganate solutions by slurried pulp samples, is an index of lignin content; kappa number $\times 0.15 =$ weight percent lignin in dry pulp. (Kappa and microkappa numbers are obtained using up to 10 grams and one gram pulp samples and the terms are used interchangeably.) Pulp viscosity, a function of average cellulose chain length and measured after dissolving pulp in an aqueous solution of cupric ethylenediamine, is an index of cellulose fiber strength. The goal of selective bleaching is to reduce the kappa number without causing a decrease in pulp viscosity. Additional experimental details are given in the figure caption. Clearly, the bleaching results with **1**, which do not yet reflect significant optimization, are comparable to the results in Figure 4A (Cl_2) and close to those shown in Figure 4B (Cl_2 and ClO_2) which reflect years of industrial optimization. Control experiments shown in Figures 4A and 4B were carried out with no POM present. The drops in viscosity associated with the control experiments are similar to those observed in the POM trials. This suggests that the drops in viscosity in the POM treated pulps are due to cellulose hydrolysis rather than to a lack of oxidative selectivity. Optimization of the time/temperature profiles of the POM treatment is expected to greatly reduce exposure of the pulp to hydrolyzing conditions. Paper sheets formed from pulps

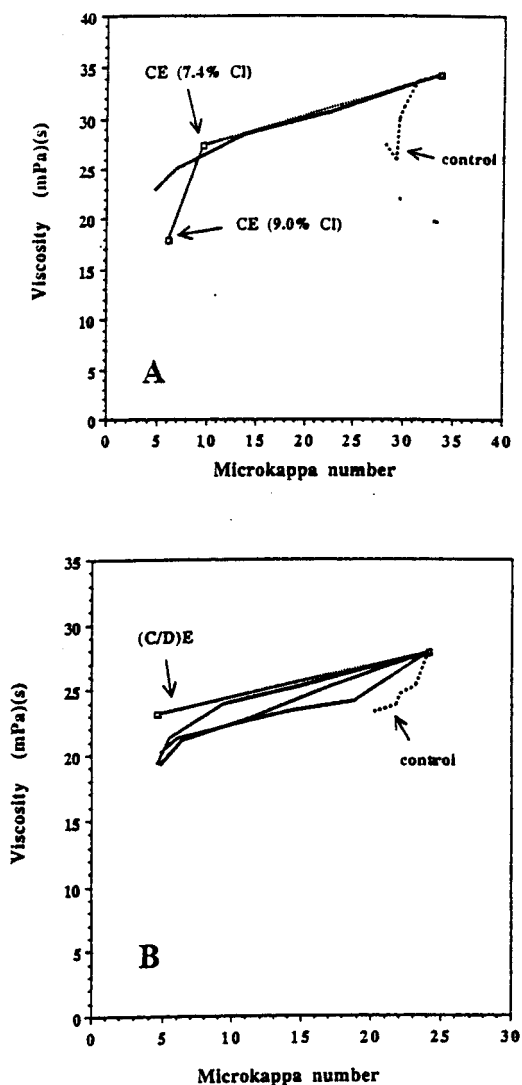


Figure 4. – Delignification of mixed-pine kraft pulps. **A:** By **1** and Cl₂. A representative softwood kraft pulp, microkappa number 33.6³³ and viscosity 34.2 mPa·s³⁴ was used. The pulp was heated for two hours at 85 °C in a solution of 1.0% aqueous NaOH under anaerobic conditions (alkali extraction), washed and dispersed in a 0.05 M solution of **1** in 0.2 M pH 7 phosphate buffer in a stirred, glass-lined, high pressure Parr reaction vessel. The mixture was flushed with N₂ gas, pressurized to 340 kPa N₂ and heated at 125 °C for 1.0 h (under these conditions **1** reacts slowly with phosphate; small amounts of [P₂W₅O₂₃]⁶⁻ and [SiV_xW_{12-x}O₄₀]^{[4+x]-}, x = 2, 3, were observed by ³¹P and ⁵¹V NMR). The pulp was then filtered and washed with water. The POM treatment was repeated two more times, each time heating at 125 °C for 2.0 h and washing with water. The treated pulps were then extracted with alkali. The multi-stage treatment was carried out three times and average values were plotted in Figure 4A. In addition, two samples of pulp were delignified using Cl₂ (7.4% and 9.0% Cl₂ on pulp) at room temperature and extracted with alkali (traditional chlorine treatment). **B:** By **1** (three trials shown) and a mixture of Cl₂ and ClO₂. Unbleached softwood kraft pulp (kappa number 24.1, viscosity 27.8 mPa·s) was delignified using **1** as in A, but without an initial alkali treatment. A second sample was delignified using a 7:3 mixture (based on electron equivalents) of Cl₂ and ClO₂³⁵ followed by alkali extraction.

delignified by treatment with **1** possess mechanical and strength properties, functions of both fiber strength and interfiber bonding, comparable to those of sheets prepared from pulps delignified using the Cl₂/ClO₂ mixture²⁴. Bleaching under similar anaerobic conditions by **2** was less effective than those by **1** or chlorine. This is likely attributable to the more negative reduction potential of **2** at pH 3 (sodium salt form)²⁵ as compared to that of **1**. Published data for pH independent anodic and cathodic potentials (vs SCE) of **1** are: E_{pa} = 0.44 V and E_{pc} = 0.35 V (wax-impregnated graphite electrode, 0.5 V min⁻¹, 5 × 10⁻⁴ M heteropolyanion, 0.1 M pH 5 acetate buffer)²². Based on additional data presented there, we estimate that the pH independent reduction potential of **2** is probably between 0.10 V and 0.20 V more negative than that of **1**.

Depolymerization of lignin by **1**

Under anaerobic conditions, **1** oxidatively degrades lignin-derived materials present in unbleached kraft pulp. During kraft pulping (sulfide catalyzed alkaline hydrolysis of lignin) alkyl aryl ether linkages, among others, are cleaved, generating phenolic end-groups in the remaining lignin polymer. Phenols, known substrates for **2**²⁶ and other POMs²⁷, are likely oxidized by **1** during anaerobic bleaching. Products of the reaction of **1** with the phenol 1-(3,5 -dimethoxy-4-hydroxyphenyl)-2-(phenoxy)propane-1,3-diol (**3**), a dimeric β-aryl ether lignin-model compound, are given in Figure 5 (see caption for experimental details). **3** reacts rapidly with **1** in water at room temperature. The reaction consumes approximately 3.1 molar equivalents of **1** and yields the ketone **4**, which results from dehydration of the benzylic hydroxyl group of **3**, and compounds **5** and **6**, which are products of cleavage at C-1 of the 3-5-dimethoxy -substituted hydroxyphenyl ring of **3**.

An analogous mixture of products was obtained upon oxidation of a closely related arylglycerol β-aryl ether lignin model compound by manganese peroxidase, a heme peroxidase excreted by the lignin degrading fungus *Planerochaete chrysosporium* which catalyzes the peroxide oxidation of Mn(II) to Mn(III)²⁸. Like **1** Mn(III) is a one electron oxidant. It was proposed that 2 equivalents of Mn(III) oxidize the phenolic moiety to a cyclohexadienyl cation that either: (i) loses a proton to give an α-ketone, or (ii) is hydrolytically cleaved to give a hydroquinone which is oxidized to the *para*-quinone by 2 additional equivalents of Mn(III) (Fig. 6). Although a wide variety of largely uncharacterized chemical structures are present in residual kraft lignin, it is entirely reasonable that anaerobic POM delignification of kraft pulps results from combinations of direct POM

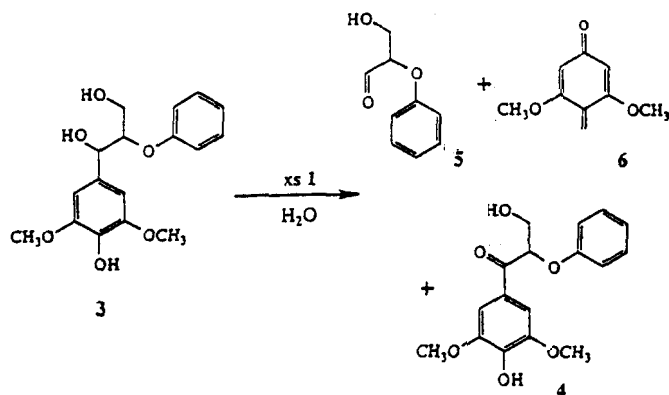


Figure 5. – Reaction of 1 with 1-(3,5-dimethoxy-4-hydroxyphenyl)-2-(phenoxy)propane-1,3-diol (3). Compound 1 (1-12 molar equivalents) was dissolved in 1 mL of 200 mM pH 5 potassium acetate buffer and flushed with N_2 in a septum covered vial. Compound 3 (2 mg), was dissolved in 20 μ L of DMF and added via syringe to the stirred solution of 1. After one hour at room temperature, the reaction was acidified with 2 N HCl and extracted 3x with a 2:1 mixture of chloroform and acetone. The organic layer was backwashed with brine, dried over $NaSO_4$, and an aliquot removed for GC/MS analysis. The remainder was concentrated to dryness, redissolved in 100 μ L of DMF and analyzed by HPLC (Hamilton PRP-1 reverse phase column with 15% acetonitrile/ H_2O /0.1% H_2PO_4 for 15 min followed by a 35 min gradient to 65% acetonitrile/ H_2O /0.1% H_2PO_4 @ 260 nm). The aqueous phase was stripped of residual volatile organics by flushing with N_2 and diluted with H_2O to a standard volume for determination of the concentration of reduced 1 by UV-vis spectroscopy (496 nm). Compound 5 was observed as the diol derivative by HPLC after $NaBH_4$ reduction of reaction products in 1:1 ethanol/ H_2O . After stirring overnight, unreacted $NaBH_4$ was quenched with saturated NH_4Cl and the mixture was extracted 3x with chloroform, washed with brine, dried with $NaSO_4$, concentrated to dryness and analyzed by HPLC as described. Borohydride reduction eliminated the peak corresponding to the ketone 4 and resulted in an increase in the relative intensity of the peak assigned to 3. Reduction also gave rise to a new peak associated with the diol derivative of the cleavage product 5. (Compound 5 was not observed in the unreduced reaction mixture). All HPLC identifications were made by comparison with authentic reference compounds and the identity of 6 was further confirmed by GC/MS.

oxidation of susceptible functional groups within the residual lignin and of heterolytic hydrolysis steps.

Wet oxidation (Unit Operation D)

Pulp bleaching by any oxidative reagent will lead inevitably to the liberation of partially oxidized organic materials derived from lignin. These byproducts constitute polluting waste and their production militates against the “closed mill”. The defensible approach at the outset to avoid these dissolved organic materials in the bleaching liquor would be to destroy them by complete oxidative mineralization (wet oxidation). To

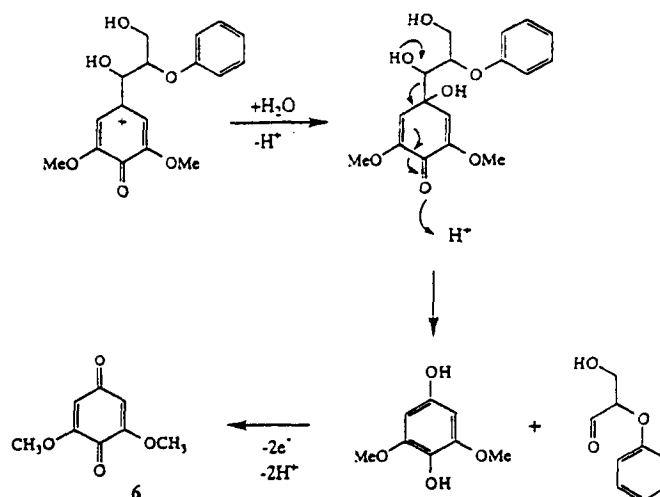


Figure 6. – Proposed mechanism of *para*-quinone formation via a cationic cyclohexadienone intermediate²⁸.

address this problem, we again turned to POMs and their chemistry. Complete mineralization of organic waste using metal oxides with and without light and/or peroxide is currently being rapidly adopted by industry as a utilitarian approach to this problem²⁹. Three points suggested that POMs might be quite effective as wet oxidation or mineralization agents. First, some POMs exhibit art extensive and reversible redox chemistry and tunable potentials. Second, a few literature reports indicated that POMs can exhibit key reactivity for mineralization, or autoxidation. the chemistry underlying oxidative mineralization. POMs are quite active at mineralizing organic materials under typical conditions of heterogeneous catalytic aerobic oxidation^{10-12,30}, and Chambers and Hill have demonstrated that POMs, under some mild reaction conditions, can be unusually effective initiators of autoxidation³¹. Third, POMs would likely be both thermally and oxidatively stable under the forcing conditions often required for effective wet oxidation.

Figure 7 illustrates the effectiveness of 2 as art agent for mineralization (see caption for experimental details). When a spent bleach liquor, prepared by anaerobic delignification of kraft pulp by 2 and containing dissolved lignin fragments, is heated in solution under O_2 at 150°C, chemical oxygen demand (COD) levels drop rapidly and then remain at a non-zero value. The recalcitrant organic compounds are initially probably acids³². These remain with the liquor during the subsequent anaerobic bleaching step, during which additional and more easily oxidized lignin fragments are dissolved. The freshly introduced

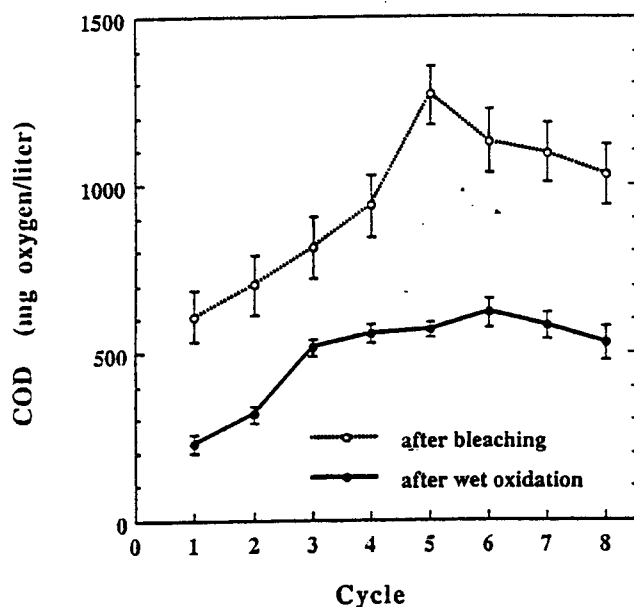


Figure 7. – Chemical oxygen demand (COD) values of POM liquors generated by the use of a single solution of **2** in eight repeated cycles of bleaching/wet oxidation. Each cycle consisted of an anaerobic bleaching reaction (3.0% by weight unbleached softwood kraft pulp, 0.05 M **2**, pH 3, 4 h at 100 °C under N₂) followed by aerobic wet oxidation of the spent bleaching liquor (0.05 M **2**, pH 3, 4 h at 150 °C under a partial pressure of 300 kPa O₂). The extent of delignification associated with each bleaching reaction was quantified by kappa number determination. After each bleaching and wet oxidation reaction, the amount of carbon dioxide produced³⁶ and the chemical oxygen demand (COD) of the organic compounds in the resultant liquor were measured³⁷. The concentration of **2** was followed titrimetrically and its integrity was measured by ³¹P NMR spectroscopy. There was no evidence for degradation of **2**.

Organic compounds, along with reduced **2**, initiate radical chain autoxidation reactions that degrade the recalcitrant

compounds left over from the previous mineralization step. The result, after several bleaching/wet oxidation cycles, is the attainment of a low steady state COD level in the recycling liquor. The amounts of CO₂ produced during the first and subsequent wet oxidation reactions remain constant. The achievement of a low steady state concentration of dissolved organics represents a net conversion of all organic compounds to carbon dioxide and water. In contrast to the impressive wet oxidation capability of **2**, **1** is ineffective. This is readily understood as the reduced form of **1** is not effectively deoxidized by O₂ under the conditions of Figure 7 whereas the reduced form of **2** is.

The principal goals of the overall effort on the title technology now are to design a POM chat is a highly selective bleaching agent, like **1**, but which is also a highly effective mineralization agent like **2**, and to continue the engineering studies necessary for optimization and integration of individual Unit Operations.

Acknowledgments

We thank the USDA Forest Service and member companies of the USDA Forest Service, Forest Products Laboratory, Polyoxometalate Bleaching Consortium for support, the Shieldalloy Metallurgical Corporation for gifts of vanadium and Osram Sylvania, Inc. for gifts of tungsten. I. A. Weinstock and K. E. Hammel thank the USDA National Research Initiative Competitive Grants Program (93-37103-9270) for support of this work.

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