POLYOXOMETALATE BLEACHING: A HIGHLY SELECTIVE, CLOSED-MILL TECHNOLOGY

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ABSTRACT

Polyoxometalates, a class of oxidatively robust inorganic oxidants and oxidation catalysts, are currently under investigation at the Forest Products Laboratory (FPL) and at Emory University as an alternative to chlorine-based chemicals in the bleaching of softwood kraft and other pulps. Although polyoxometalate salts are used in a number of industrial processes, the feasibility of using these salts and oxygen in the commercial bleaching of chemical pulps was only recently demonstrated. A clear advantage of polyoxometalates over oxygen alone, hydrogen peroxide or ozone, is their inherently high selectivity for the residual lignin in softwood kraft pulps. Softwood kraft pulps delignified to low kappa numbers using polyoxometalates possess papermaking properties comparable to those obtained using chlorine (and/or dioxide) and alkali. The goal of ongoing research is to develop a highly selective, energy-efficient, oxygen-based polyoxometalate delignification and bleaching technology, compatible with mill closure. To this end, several unit operations are under development with the aim of constructing and optimizing an integrated, laboratory-scale bleaching facility. These include: Bleaching, pulp washing, wash water recovery, removal of salt impurities, wet oxidation of dissolved organic compounds, and aerobic oxidation of spent polyoxometalate salts to their bleaching active forms.

INTRODUCTION

Background

The discharge of persistent and bioaccumulative toxic waste is perhaps the most pressing environmental problem currently facing the pulp and paper industry worldwide. Although chlorine and its compounds are the most effective chemicals currently available for bleaching chemical wood pulps or recycled paper, the use of these oxidants results in the generation of a variety of chlorinated organic compounds. For example, it is estimated that roughly 83 million kilograms of adsorbable organic halides (AOX) will be generated by U.S. pulp bleaching operations in 1995. These chlorinated organics that survive waste water treatment at the mill are eventually released into the environment. Many of these are persistent and bioaccumulative. Although the toxicities of the majority of these organic halides are unknown, some are known to be extremely toxic and many others are suspect. The challenge is, thus, to eliminate the need for bleaching chemicals that produce persistent toxic byproducts. In addition, many in the pulp and paper industry expect that the release of any organic waste (other than carbon dioxide) into the environment will eventually be banned altogether. There is thus an additional need for the development of an effluent-free “closed” bleach mill from which few or any chemical waste-products, other than carbon dioxide and water, are released [1].

The search for an acceptable alternative to chlorine and chlorine compounds for bleaching softwood kraft pulps is the subject of an intensive international effort that began over two decades ago. Despite this effort, no widely acceptable alternative is currently available. The goal of the United States Department of Agriculture (USDA) Forest Service, Forest Products Laboratory’s Polyoxometalate Bleaching Program is to develop an effective, commercially attractive and totally chlorine free (TCF) bleaching technology compatible with mill closure [2]. The Polyoxometalate Bleaching Program is a collaborative effort involving the Forest Products Laboratory (FPL), Emory University and the University of Wisconsin-Madison. Current support is provided by the USDA through the Cooperative State Research Service, the USDA Forest Service, and by an international consortium of industrial partners established in March, 1994.

As currently envisioned, an effluent-free polyoxometalate bleaching mill will consist of four unit operations: Bleaching: Pulp washing; Concentration of wash water and removal of undesired inorganic salts; and Regeneration of the polyoxometalate (POM) to its bleaching-active form with simultaneous oxidative removal of dissolved organic materials. Laboratory demonstration of the viability of the unit operations most critical to the successful performance of the new technology has recently been completed at the FPL and three U.S. patent applications, covering the novel chemical processes and engineering concepts developed in the course of the Bleaching Program, have been filed jointly by FPL and Emory University [3].

Project History

Prior to inception of the Polyoxometalate Bleaching Program, it was recognized that oxygen, the least expensive alternative to chlorine or chlorine dioxide, would be the oxidant of choice for commercial applications. It was also felt that the best way to control the reactivity of oxygen would be through the introduction of transition metal catalysts. This approach was suggested by the role transition metal ions play in the selective degradation of lignin by wood-rotting fungi. In this biological system, a chain of events catalyzed by metal-containing enzymes and complexes results in the net degradation of lignin by oxygen. At the outset of the FPL Bleaching Program, these natural, transition-metal-catalyzed processes served as a paradigm in the search for a new, selective, economically-viable, and environmentally-friendly bleaching technology.

In general, the activity of transition metal ions in water is often difficult to control. In the biodegradation of lignin, these problems are overcome by the use of well-behaved metalloenzymes and transition metal complexes. Indeed, biomimetic bleaching systems have been prepared using metalloenzyme models such as synthetic metalloporphyrin complexes [4]. Unfortunately, these synthetic organic complexes are expensive and inherently susceptible to oxidative degradation during bleaching. Large scale commercial bleaching, however, will require the use of oxidatively robust transition metal complexes that can be easily prepared from inexpensive materials. In addition, they must be stable at elevated temperatures so that rates which we prerequisite for large scale commercial operations can be achieved. Polyoxometalate complexes meet these criteria. They are remarkably stable to oxidizing conditions and include a wide variety of water-soluble inorganic compounds, many of which are easily prepared from common, non-toxic mineral ores.

POLYOXOMETALATES

Polyoxometalates are discrete polymeric anions that form
spontaneously when simple oxides of vanadium, niobium, tantalum, molybdenum or tungsten are combined under the appropriate conditions in water [5]. In a great majority of polyoxometalates, the transition metals are in the d electronic configuration which dictates both a high resistance to oxidative degradation and an ability to oxidize other materials such as lignin. The principal transition metal ions that form polyoxometalates are tungsten(+6), molybdenum(+6), vanadium(+5), niobium(+5) and tantalum(+5).

Isopolymetolates, the simplest of the polyoxometalates, are binary anions of the formula $[M_nO_{m}¥]$ where m may vary from two to over 30. Heteropolyoxometalates have the general formula $[XM_{m}O_{n}¥]$ and possess a heteroatom, X, at their center. A variety of main group and other elements can serve as heterostems. For example, in the Keggin structure $[\alpha-PW_{12}O_{40}¥]$, X is phosphorus, P(+5). The central phosphorus atom is surrounded by twelve WO$_{6}$ octahedra. The polyoxometalate anions can be prepared in either acid or salt forms, both of which are water soluble.

Removal of a (M=O)$_n$ moiety from the surface of the Keggin structure $[\alpha-\{XM_{m}O_{n}¥\}]$, where M is Mo(+6) or W(+6) and X is P(+5) creates the "lacunary" polyanion, $[\alpha-\{XM_{m}O_{n}¥\}]$. The lacunary complex acts as a pentadentate ligand for redox active transition metal ions, such as vanadium(+5) in $[\alpha-\{PW_{12}O_{40}¥\}]$. Further substitution is also possible, giving anions of the form $[X_{m+1}M_{m}O_{n}¥]$, such as $[\alpha-\{PV_{2}Mo_{5}O_{19}¥\}]$ where M is V(+5) and M is Mo(+6). In place of vanadium(+5), d-electrons containing redox active transition metal ions may also be used, giving complexes such as $[\alpha-\{S Mn(+3)OH_{2}W_{12}O_{39}¥\}]$, which contains a manganese(+3) ion. The lacunary heteropolyanions stabilize the active metal ions in solution and control their reactivity [6].

In bleaching, the POMs are highly selective yet have a distinct kinetic advantage over molecular oxygen [7,8]. Due to thermodynamic considerations, however, many POMs also have the attractive property that after use in bleaching, the reduced polyoxometalates can be reoxidized with oxygen. This means that POMs can be employed as reusable agents in repeated cycles of pulp bleaching followed by regeneration (reactivation) of the spent bleaching liquor with oxygen.

During POM bleaching residual Kraft lignin fragments, and some polysaccharides, are dissolved by the polyoxometalate bleaching liquor. To achieve mill closure, it is thus necessary to remove the dissolved lignin fragments and polysaccharides. One possibility, already demonstrated in the laboratory, is that, simultaneous with their regeneration, 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.

**CLOSED MILL POLYOXOMETALATE PROCESS**

As currently envisioned, an effluent-free POM bleaching mill 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 (Figure 1).

Bleaching and the regeneration of used bleaching liquors are each carried out in separate steps [3,7]. In the bleaching step (eq. 1) mixtures of water, pulp and a fully oxidized POM ($P_{ox}$) are heated in a sealed vessel. During the reaction, the POM is reduced ($P_{red}$) as residual lignin in the pulp is oxidized. Batch bleaching reactions performed to date demonstrate that POM delignified pulps possess papermaking properties closely resembling those of chlorine or chlorine dioxide delignified pulps [9]. After the reaction, the spent bleaching liquor is separated from the pulp and, prior to reuse, is reoxidized by exposure to oxygen (eq. 2).

\[ P_{ox} \rightarrow P_{red} \]

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


Fig. 1. Proposed flow diagram for a polyoxometalate bleaching process, including the possible need for a final P stage.