Zeolites in Pulp Bleaching

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This thesis is a summary and discussion of results presented in the papers listed below. In the text they are referred to by their Roman numerals I-III.

**Paper I**  
Effects of Zeolite Addition on the Manganese Catalysed Decomposition of Hydrogen Peroxide.  
Kurt Dyhr and Johan Sterte.  

**Paper II**  
Use of Zeolites in Hydrogen Peroxide Bleaching of Pulp.  
Kurt Dyhr and Johan Sterte.  

**Paper III**  
Use of Zeolites To Inhibit The Transition Metal Catalysed Decomposition of $\text{H}_2\text{O}_2$ in the Bleaching of Pulp.  
Kurt Dyhr and Johan Sterte.  
Submitted to 12th International Zeolite Conference, Baltimore, Maryland, USA, July 5-10, 1998.
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4. Summary of this work

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4.5 Investigation of the pH-drop

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6. Further developments

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Paper I

Paper II

Paper III
1. Introduction

Mainly due to environmental considerations, most manufacturers of pulp have phased out the use of elementary chlorine in their bleaching processes. In order to minimize the amount of chlorinated organic substances in the bleaching effluents or to completely avoid the formation of such substances, processes have been developed using bleaching agents such as chlorine dioxide, ozone, hydrosulfite and hydrogen peroxide. Bleaching without the use of chlorine containing chemicals, usually termed TCF (totally chlorine free)-bleaching, generally involves a sequence of operations including one or more treatments with alkaline hydrogen peroxide. A problem associated with the use of hydrogen peroxide for this application is that some transition metal substances are very efficient in catalyzing the decomposition of the peroxide. The mechanism of metal catalysed hydrogen peroxide decomposition is not completely clear. A suggestion is that the decomposition of hydrogen peroxide could go through two different types of mechanism; One type involves different free radical mechanisms (Colodette et al., 1988, Gierer and Jansbo, 1993) which mainly produces hydroxy- or superoxide anion radicals. The other one is a two consecutive one electron transfer step mechanism (Colodette et al., 1988, Gierer and Jansbo, 1993) which mainly produce water and oxygen. Both mechanisms prevent effective use of the peroxide for bleaching of the pulp and the free radical mechanism also degrades carbohydrates and contributes to the discoloring of the pulp.

The pulp contains trace amounts of transition metal ions (Mn, Fe and Cu) introduced mainly with the raw material. Among the transition metals, manganese seems to have the most deleterious effect on peroxide stability. This is due to a higher level of Mn than copper and iron and also because the copper and iron ions are more complexed with the wood components (Colodette and Dence, 1989b). The manganese level in wood is generally around 100 ppm (calculated on dry pulp), the exact amount mainly depending on geological conditions in the area where the trees used as raw material were grown.

Before the bleaching process, manganese is mainly present in the form of Mn$^{2+}$-ions in mechanical pulp. Kraft pulp is usually pretreated in an oxygen step before peroxide bleaching. It is not clear in what oxidation state manganese is after an oxygen stage but an investigation (Brelid et al., 1995) showed that 90-95% of the manganese could be removed by ion
exchange with Ca and Mg ions at pH 4.5 from an oxygen bleached softwood kraft pulp indicating that Mn is in a cationic form, i.e. Mn$^{2+}$. In the bleaching process, at high pH (> 10) under oxidizing conditions, Mn is oxidized mainly into insoluble manganese oxides and hydroxides. The oxides and hydroxides acts as very potent catalysts for the decomposition of hydrogen peroxide. Presently, this problem is handled by the use of a chelating step (Q-step) prior to peroxide bleaching. In this step a chelating agent such as EDTA or DTPA is used for chelation of the transition metals. The chelated transition metals are then washed out with the chelation agent in a washing step before the bleaching step. The chelating agents also have a positive effect on the bleaching result even without the washing step and this step is sometimes excluded. This operation is called direct addition, but is not commonly used because it is less effective than an operation with a washing step. The chelating agents used are, however, questionable from an environmental standpoint. They are known to be non-biodegradable or only very slowly degraded in natural waters. This and their strong affinity for some heavy metal ions has resulted in a suspicion that they may solubilize heavy metals from sediments and thus affect the eco-system in a negative manner. This, in turn, has resulted in increased restrictions on the industrial use of chelating agents and has created a strong incentive for the pulp and paper industry to find alternative materials or processes through which this problem can be handled.

One such alternative which has been proposed and which is the focus of the present work is to substitute the chelating agents with zeolites.
2. Background

2.1 The chemistry of hydrogen peroxide.

Hydrogen peroxide is an oxidizing bleaching agent widely used for bleaching of chemical, and mechanical pulps as well as deinked paper. All of the hydrogen peroxide in the bleaching stage is not consumed in bleaching reactions; there is a large amount consumed in decomposition reactions.

2.1.1 Hydrogen peroxide decomposition mechanisms.

The equilibrium between hydrogen peroxide and the perhydroxyl anion (HO₂⁻) in alkaline conditions is:

\[
H_2O_2 + OH^- = HO_2^- + H_2O
\]  

(1)

Under acidic conditions and free from impurities, hydrogen peroxide is remarkably stable and can be stored for months with negligible loss. Under alkaline conditions or in the presence of transition metals, hydrogen peroxide starts to decompose (Lapierrre et al., 1995).

In the absence of transition metal ions in alkaline solutions the mechanism for decomposition of hydrogen peroxide is a base catalysed one. The exact mechanism is not clear. The rate of the base catalysed decomposition of hydrogen peroxide is much lower than that of the transition metal catalysed decomposition.

As indicated above there is also a consumption of hydrogen peroxide through a transition metal ion induced decomposition by Mn²⁺, Fe²⁺ and Cu²⁺ ions. The mechanism of metal catalysed hydrogen peroxide decomposition is not completely clear either. It seems that the decomposition catalysed by those cations can proceed through two types of redox processes catalysed by transition metal species. The first type involves a one electron reduction of hydrogen peroxide with the formation of hydroxy- and superoxide anion radicals and is believed to dominate for mononuclear transition metal ion complexes. The second type is a
heterogenous surface-catalysed process caused by colloidal polynuclear transition metal oxides/hydroxides and proceeds mainly by two consecutive one-electron transfer steps. This decomposition mode produces molecular oxygen and water but no free hydroxyl radicals (Gierer and Jansbo, 1993). The influence of specific transition metals on peroxide decomposition is further discussed below.

### 2.1.2 Peroxide bleaching chemistry.

The active species in the alkaline hydrogen peroxide is the perhydroxyl anion (\( \text{HO}_2^- \)) which reacts within the lignin polymer network to open ring systems or to cleave side chains (see figure 1). As a result, the extended conjugation of the \( \pi \)-electron system is destroyed. The absorption of light is shifted from longer to shorter wavelengths causing an increase in brightness (Süss et al., 1991).

The bleaching of mechanical pulps with alkaline hydrogen peroxide leads to the destruction of chromophoric structures with only a minor decrease in pulp yield (Gellerstedt et al., 1981).

Bleaching of chemical pulps to high brightness requires elimination of the chromophoric structures by the perhydroxyl anion (\( \text{HO}_2^- \)) and a substantial removal of lignin, through degradation/dissolution, by reaction with hydroxy- and superoxide anion radicals. The reactivity of hydroxy- and superoxide anion radicals towards aromatic lignin (phenolic structures) is only slightly higher than that towards cellulose. Therefore if hydrogen peroxide decomposes too fast by transition metal induced catalytic reactions, the concentration of hydroxy- and superoxide anion radicals become too high and the selectivity towards lignin is lost and cellulose degradation occurs (Lapierrre et al., 1995).
Figur 1. Examples of reactions between the perhydroxyl anion (HO₂⁻) and the a chromoforic group in the lignin framework (Hafner et al., 1990).

2.2 The influence of different metal ions in the pulp

The pulp contains different metal ions which are mainly introduced with the raw material. The exact amount of the metal ions mainly depends on geological conditions in the area where the trees used as raw material were grown, recirculation of streams in the bleaching plant, erosion from the process equipment and addition of magnesium into the bleaching plant. In table 1 are the contents for the most important metal ions which have an influence on alkaline hydrogen peroxide bleaching listed for a spruce TMP (thermo mechanical pulp) pulp and an oxygen bleached kraft pulp. It is well known that hydrogen peroxide is very sensitive to the transition metals (Mn, Fe and Cu) because these metals act as catalysts and decompose hydrogen peroxide. Calcium and especially magnesium have a positive impact on alkaline hydrogen peroxide bleaching. A good metal ion profile for hydrogen peroxide bleaching should have as low concentration of the transition metal ions (Mn, Fe and Cu) as possible, and a high content of magnesium and calcium. The influence of the transition metals, calcium, magnesium and sodium is further discussed below.
<table>
<thead>
<tr>
<th>Ions</th>
<th>Mechanical pulp (TMP)</th>
<th>Kraft pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>800 ppm</td>
<td>3800 ppm</td>
</tr>
<tr>
<td>Ca</td>
<td>1800 ppm</td>
<td>1247 ppm</td>
</tr>
<tr>
<td>Mg</td>
<td>130 ppm</td>
<td>156 ppm</td>
</tr>
<tr>
<td>Cu</td>
<td>4 ppm</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Fe</td>
<td>15 ppm</td>
<td>6 ppm</td>
</tr>
<tr>
<td>Mn</td>
<td>100 ppm</td>
<td>70 ppm</td>
</tr>
</tbody>
</table>

**Table 1.** Approximate levels of cations in a mechanical (TMP)- and a kraft pulp.

### 2.2.1 Manganese

Manganese is the most prevalent transition metal in the pulp. The content is generally around 100 ppm and manganese is not bound with the fibers. Mainly due to the high content, manganese is usually considered to be the most deleterious of the transition metals. Collodette et al. (1988) investigated the decomposition of hydrogen peroxide in the pH-range 9.8 to 11.8 and reported a maximum decomposition of hydrogen peroxide at pH 9.8. Other investigators have also reported an increase in the decomposition of hydrogen peroxide at pH 9.5 compared with higher pH values (Galbács and Csaná, 1983). Thus manganese would seem to have an increased influence on the decomposition at lower pH (< 9.8). This is a problem in bleaching of mechanical pulps, because of the initial pH-drop during the process, the pH usually declines very rapidly below 10 (Collodette et al., 1988). Different mechanisms have been proposed for the manganese decomposition of hydrogen peroxide. One type of proposed mechanisms is a radical induced reaction (Walling, 1975) and another type involves a two consecutive one-electron transfer steps and this heterogenous surface catalyzed reaction is caused by colloidal transition metal oxides/ hydroxides (Gierer and Jansbo, 1993). Colodette
et al. (1988) measured the formation of hydroxyl and superoxide radicals in alkaline solutions with manganese and hydrogen peroxide. Manganese caused catalytic decomposition of hydrogen peroxide but only a small amount of radicals (Collodette et al., 1988). A similar result was obtained by Gierer et al. (1993). It therefore appears that the active species for manganese decomposition of hydrogen peroxide is collodial manganese oxides/hydroxides and that the most important type of mechanism for decomposition of hydrogen peroxide is a surface catalysed two consecutive one-electron transfer steps reaction (Gierer and Jansbo, 1993).

2.2.2 Iron

For mechanical pulps it seems that iron is strongly attached to the lignin and carbohydrate components. An investigation of a TMP showed that 75 % of the iron is strongly attached to the fibers (Collodette and Dence, 1989b). The iron which is attached to the lignin and carbohydrate components showed no catalytic activity for the decomposition of hydrogen peroxide. Iron catalyses the decomposition of hydrogen peroxide and the catalytic effect increases with pH, especially above pH 10.8 (Collodette et al., 1988). An investigation of the formation of radicals in alkaline hydrogen peroxide solutions containing iron ions by Collodette et al. (1988) showed that the formation of radicals was small. A similar result was obtained by Gierer and Jansbo (1993). Goetite (α–FeOOH) has been proposed to be the active species for hydrogen peroxide decomposition in hydrogen peroxide bleaching when iron is present (Collodette et al., 1988). This would explain why the decomposition of hydrogen peroxide only produces small amounts of radicals.

2.2.3 Copper

The fraction of copper which is strongly attached to the lignin and carbohydrate components has shown no catalytic activity for the decomposition of hydrogen peroxide (Collodette and Dence, 1989b). Free copper ions catalyse the decomposition of hydrogen peroxide and the catalytic effect increases with pH especially above pH 10.8 (Collodette et al., 1988). According to Collodette et al. (1988) and Gierer and Jansbo (1993) a large amount of radicals is produced when hydrogen peroxide is decomposed in the presence of copper. It therefore
seems that the main mechanism for the catalytic decomposition of hydrogen peroxide by copper is a radical one.

### 2.2.4 Magnesium

Today magnesium is used as an additive in oxygen and peroxide bleaching. In peroxide bleaching of kraft pulp an addition of magnesium gives the following advantages: higher brightness, lower consumption of hydrogen peroxide and lower degradation of carbohydrates (Bergnor et al., 1994). In oxygen bleaching magnesium is used as a protective agent against carbohydrate degradation. The exact mechanism for how magnesium acts as a stabilizer of hydrogen peroxide and as a protector against carbohydrate degradation is not clear. In a hydrogen peroxide solution with copper or iron, magnesium acts as an inefficient stabilizer and in a solution with manganese an addition of magnesium gives a catalytic effect (Collodette et al., 1989a). Magnesium in combination with manganese only has an stabilizing effect on hydrogen peroxide solutions in the presence of wood pulp or a lignin model such as the anionic polymer polygalacturonic acid (Abbot et al., 1992, Lidén and Öhman, 1997). Lidén and Öhman (1997) found that manganese and magnesium precipitate as solid compounds like (Mg, Mn)(OH)$_2$(s,s) and (Mg, Mn)CO$_3$(s,s) and manganese is thus deactivated in those compounds and that the function of the wood pulp or anionic polymer is to change the physical characteristics of these precipitates into a negatively charged colloidal phase. Lindeberg (1994) investigated how the ratio between Mg/Mn influences peroxide bleaching on oxygen bleached birch kraft pulp. It was shown that a ratio of Mg/Mn > 30 mol/mol gave maximum brightness and that a Mg/Mn ratio over 50 mol/mol also gave the highest viscosity, minimum consumption of hydrogen peroxide and the minimum kappa number. According to Devenyns and Plumet (1994) the optimal ratio between Mg/Mn for a mechanical pulp is 23 mol/mol. The optimum ratios of Mg/Mn for chemical and mechanical pulps is of course dependent on the composition of the pulps and the bleaching conditions.

### 2.2.5 Calcium

A high content of magnesium and calcium ions, decrease cellulose degradation and the loss of strength in kraft pulp bleaching (Ek et al., 1994). A high content of calcium ions could also decrease the chelation of transition metals for chelating agents (see chapter 2.3). The high
level of calcium ions compared with those levels of transition metal ions (see table 1) could also have a negative influence on the zeolites ability to chelate transition metal ions.

2.2.6 Sodium

As seen in table 1, the content of sodium (Na) is much higher in the chemical pulp compared with the TMP pulp. Divalent ions such as the transition metals, magnesium and calcium ions are usually easier to ion exchange into the zeolite compared with monovalent ions such as sodium. But the high level of sodium ions (nearly 4000 ppm) and the fact that the ion strength is much higher in the chemical pulp, could have a negative influence of the ion exchange selectivity for the transition metals, when they are ion exchanged into the zeolite.

2.3 Chelating agents

The most common chelating agents used in the pulp industry today are the sodium salts of DTPA (diethylenetriaminepentaacetic acid) and EDTA (ethylenediaminetetraacetic acid) (Lapierre et al., 1995). According to Dow chemical company other chelating agents that are also used in the pulp industry are the sodium salts of HEDTA (N-(hydroxyethyl)-ethylenediaminetriacetic acid), NTA (nitrilotriacetic acid) and DTMPA (diethylenetriaminepentamethylene-phosphonic acid) (Dow, 1993). Chelating agents have higher selectivities for the transition metals (Mn, Fe and Cu) than for calcium and magnesium and are used to control the metal ion profile in the pulp (Lapierre et al., 1995).

Cations are surrounded by anions or neutral molecules. The groups immediately surrounding a cation are called ligands, and can be considered as electron pair donors. Ligand molecules may contain two or more atoms which can simultaneously form a two electron donor bond to the same cation. Such ligand molecules are called polydentate ligands or chelates (from the Greek word meaning to claw), as they appear to grasp the cation between the donor atoms. Bidantate, tridentate, quadridentate, etc., are terms used to designate chelating agents (chelants) with two, three, four, etc., binding sites. An example of a chelate with six binding sites is shown in figure 2. Bonding between the electron-donating chelating agent and the electron-accepting metal may range from essentially ionic to essentially covalent. Electron donor groups include oxygen, nitrogen and, to a lesser degree, sulphur. In figure 3 the structures of EDTA and DTPA are shown with their binding sites. The strength of the
complexing between the chelating agent and metal ion is considerable (Lapierre et al., 1995). According to Dow chemical company this strong complexation is partly dependent on the number of active sites in the chelating agent and how many sites to which the metal ion can coordinate. NTA has four sites, EDTA has six, and DTPA has eight sites. Many metal ions can coordinate to more than six chelating agent sites. This explains why NTA forms less stable complexes with certain metal ions than those of EDTA and DTPA.

The equilibrium constant for the reaction between the metal ion and the chelating agent is a measure of the affinity of the chelating agent for the metal ion.

\[
M^{n+} + EDTA^{4-} \rightarrow MEDTA^{(4-n)-}
\]  

\( K_S = [MEDTA^{(4-n)-}] / [M^{n+} \cdot EDTA^{4-}] \)  

The log K-value provides a measure of the extent to which the metal ions react with the chelating agent at equilibrium. Another important factor is the pH. At low pH values there is a competition between hydrogen ions and metal ions for binding to the chelating agent. At high pH values there is a competition between the chelating agent and hydroxide ions for metal ions. Many metal oxides/hydroxides have low solubility products. Chelating at the right pH is important when using chelating agents in pulp bleaching. For example the optimal pH for chelating with EDTA is pH between 5-6 (Bryant et al., 1993).

The higher oxidation states of manganese (III) and (IV) are rapidly reduced by the chelating agents EDTA and DTPA in slightly acidic solutions whereas iron compounds are not reduced. This implies that manganese precipitates, in contrast to iron precipitates, can be easily removed from the pulp in a chelating treatment stage (Lidén and Öhman, 1997).

The influence of other anions on the chelating agent is normally small. According to Dow chemical company one exception is the sulfide ion. Metal sulfides are extremely insoluble which explains why the chelating agent is less effective when appreciable amounts of sulfide ions are present in the pulp.

The most common way to use chelating agents in pulp bleaching is to have a pretreatment stage and wash out the chelating agent and the transition metals before the bleaching stage (Lapierre et al., 1995).
Chelating agents deactivate the catalytic effect of the transition metals on decomposition of hydrogen peroxide. A direct addition of the chelating agent into the bleaching plant would allow a less complex bleaching plant because the washing stage (press stage) would not be required. In the bleaching plant the pH is high and at high pH the chelating agents create complexes with calcium and magnesium ions (Wennerström and Ulmgren, 1994), whereas the transition metals could be bound as oxide/hydroxides. Therefore one would be forced to add an excess of chelating agents during direct addition of the chelating agent. An additional problem with this method is that some transition metals in higher oxidation states, for example Fe$^{3+}$ and Mn$^{4+}$, can cause decomposition of hydrogen peroxide even if they are chelated (Gellerstedt and Agnemo, 1980).

Figure 2. Chelating agent-metal ion structure (EDTA-cobalt). Heavy shading metal; solid, nitrogen; light shading, carbon; no shading, oxygen. Hydrogen atoms are not shown (Lapierre et al., 1995).
2.4 Zeolites

There are about 30 natural Zeolites and the number of synthetized ones is about 150 (Breck, 1984). Zeolites are porous, crystalline, aluminosilicates with a three dimensional framework which consists of an assemblage of AlO₄ and SiO₄ tetrahedra. These tetrahedra are joined together in various regular arrangements through shared oxygen atoms to form an open crystal lattice consisting of defined channels and cages (Breck, 1984). Zeolites have pores of uniform size (3 A to 10 A) (Robinson et al., 1991) which are uniquely determined by the unit structure of the crystal. These pores will completely exclude molecules which are larger than their diameter (Robinson et al., 1991). The aluminia atoms in the zeolites give the zeolite its ion exchange capacity towards cations and the defined pores gives the zeolite selectivity towards different ions when they are ion exchanged into the zeolite. Zeolites have a large ion-exchange capacity.
capacity and are used in detergent powders to remove calcium ions from laundry water. Zeolites are thermostable. Synthetic zeolites have a high brightness, 94-99% in ISO-brightness, and are also chemically stable in the pH-range from about 4.5 to 12. Zeolites are manufactured and used in powder form. The powder consists of particles with a diameter from about a half to a few microns.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Structural formula</th>
<th>CEC (meq/g)</th>
<th>brightness (ISO-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2 SiO₂ Al₂O₃ Na₂O</td>
<td>7.0</td>
<td>96.6</td>
</tr>
<tr>
<td>P</td>
<td>2 SiO₂ Al₂O₃ Na₂O</td>
<td>7.0</td>
<td>98.6</td>
</tr>
<tr>
<td>Y</td>
<td>5.3 SiO₂ Al₂O₃ Na₂O</td>
<td>4.1</td>
<td>98.6</td>
</tr>
<tr>
<td>M10A</td>
<td>13 SiO₂ Al₂O₃ Na₂O</td>
<td>2.1</td>
<td>94.4</td>
</tr>
</tbody>
</table>

*a* Calculated from elemental analyses provided by manufacturers.  
*b* Calculated for dehydrated zeolites from structural formula.

Table 2. Structural formula, CEC and brightness for different zeolites.

2.4.1 Ion exchange characteristics of the zeolites

The cation exchange behavior of zeolites depends on (1) the nature of the cation species, the cation size, both anhydrous and hydrated and cation charge; (2) the temperature; (3) the concentration of the cation species in solution; (4) the anion species associated with the cation in solution; (5) the solvent (most exchanges have been carried out in aqueous solutions, although some work has been done in organic solvents) and (6) the structural characteristics of the particular zeolite (Breck, 1984).

The ion exchange selectivity, sieving or partial sieving of zeolites toward various cations have been attributed to one or more of three possible mechanisms; (1) the cation may be too large to enter smaller channels and cavities within the zeolite structure, or in some zeolites the exchangeable cation is locked in during synthesis, e.g., potassium ions in zeolite L, and cannot be replaced, (2) the distribution of charge on the zeolite structure may be unfavorable for the
cation, (3) the size of the hydrated cation in aqueous solution may influence and retard exchange of the cation since an exchange of solvent molecules must occur for the cation to diffuse through apertures which are to small to accommodate the solvated cation (Breck, 1984). The zeolite also contains different ion exchange sites. For instance in zeolite A there are three different ion exchange sites, SI, SII and SIII and different ions prefer different sites. According to an investigation by Förster and Witten (1988) it seems that Mn$^{2+}$ prefer to occupy the SI site in zeolite A.

### 2.4.2 Ion exchange capacity

The ultimate base exchange capacity of a zeolite depends on the chemical composition; a higher exchange capacity is observed with zeolites of low SiO$_2$/Al$_2$O$_3$ ratios (see table 3). In aqueous solutions, the relevant capacity is that of the hydrated zeolite. In many cases the measured exchange capacities deviate from these values due to impurities (as in mineral zeolites) or variation in chemical composition. The specific exchange capacities vary with the exchange cation.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>SiO$_2$/Al$_2$O$_3$</th>
<th>milliequiv/g</th>
<th>milliequiv/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anhydrous</td>
<td>Hydrated</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chabazite</td>
<td>2</td>
<td>5</td>
<td>3.9</td>
</tr>
<tr>
<td>Mordenite</td>
<td>5</td>
<td>2.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Erionite</td>
<td>3</td>
<td>3.8</td>
<td>3.1</td>
</tr>
<tr>
<td>Clinoptilo</td>
<td>4.5</td>
<td>2.6</td>
<td>2.2</td>
</tr>
<tr>
<td>-lite</td>
<td>4.5</td>
<td>2.6</td>
<td>2.2</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>1</td>
<td>7.0</td>
<td>5.5</td>
</tr>
<tr>
<td>Zeolite X</td>
<td>2.0</td>
<td>5.0</td>
<td>4.7</td>
</tr>
<tr>
<td>Zeolite T</td>
<td>3.5</td>
<td>3.4</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 3. Exchange Capacity of various Zeolites (Breck, 1984).
2.4.3 Ion exchange selectivity for different zeolites.

As the thesis is focused on the effects of manganese, this part is primarily directed on the ion-exchange towards manganese. Zeolites usually have a higher selectivity for exchange of calcium ions compared with manganese. For zeolite A which is the most extensively studied zeolite for use in pulp bleaching (von Raven et al., 1989, von Raven et al., 1991, Leonhardt et al., 1993, Sain and Denault, 1996, Rivard et al., 1997) the following selectivity series are shown for comparison: Zn > Sr > Ba > Ca > Co > Ni > Cd > Hg > Mg (Breck, 1984) and Pb > Ag > Cu > Cd > Zn > Co > Ni > Mn (Stoveland and Lester, 1980). The high selectivity for calcium ions could be a problem when using zeolites in pulp bleaching because the levels of calcium ions are higher compared with the levels of transition metals in the pulp (see chapter 2.2, table 1). A high ratio between Mg and Mn has a positive influence on the bleaching result (Lindeberg, 1994, Devenyns and Plumet, 1994), (see chapter 2.2.4). In table 4 the selectivity series is summarized from the literature for different zeolites and different cations. As can be seen from table 4 only one, the P type zeolite has a higher selectivity for manganese compared with magnesium and could be used to increase the ratio between Mg and Mn in the bleaching stage. But the selectivity series in table 4 does not consider the influence of different factors like that the pulp is an weak ion exchanger (Devenyns et al., 1994) and that the selectivity and how hard the ions are bound to the pulp is dependent on pH and temperature.

2.4.4 An economic comparision of zeolite A with EDTA and DTPA.

Zeolite A is the most common zeolite on the market and is used to remove calcium ions from laundry water. Zeolite A and zeolite P are the zeolites which have the highest chelation capacity among the zeolites. As seen in table 5 the chelation capacity for zeolite A is nearly 75 % higher compared with EDTA and DTPA. The chelation cost for zeolite A is nearly 40 % lower compared with DTPA and nearly 30 % lower compared to EDTA. An normal addition of the conventional chelating agents EDTA and DTPA are in the range 0.2-0.5 wt% and the addition of zeolite presented in the investigations (von Raven et al., 1989, von Raven et al., 1991, Leonhardt et al., 1992, Sain and Denault, 1996, Rivard et al., 1997) from the literature is in the range from 1 to 4 wt% for zeolite A. A calculation on weight basis shows that the cost for using zeolite A on weight basis is higher compared with the chelating agents EDTA and DTPA and then are not different kinds of additives included. Other economic advantages
(see Chapter 2.5) with zeolites like decreased consumption of sodium hydroxide, lowered COD-levels and the fact that the zeolite could be used as a filler in the paper is not estimated here.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Selectivity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pb &gt; Ag &gt; Cu &gt; Cd &gt; Zn &gt; Co &gt; Ni &gt; Mn</td>
<td>(Stoveland and Lester, 1980)</td>
</tr>
<tr>
<td>A</td>
<td>Pb &gt; Ag &gt; Cu &gt;&gt; Cd &gt; Zn &gt;&gt; Co, Ni, Mn</td>
<td>(Manuel et al., 1981)</td>
</tr>
<tr>
<td>A</td>
<td>Pb &gt; Ag &gt; Cu &gt;&gt; Cd &gt; Zn &gt; Hg</td>
<td>(Manuel et al., 1981)</td>
</tr>
<tr>
<td>A</td>
<td>Cu &gt; Cr, Zn, Pb &gt; Cd &gt; Ni</td>
<td>(Manuel et al., 1981)</td>
</tr>
<tr>
<td>A</td>
<td>Cu &gt; Cd &gt; Mg, Zn &gt; Mn &gt; Co &gt; Ni</td>
<td>(Shatirishvili and Zautashvili, 1981)</td>
</tr>
<tr>
<td>P</td>
<td>Pb &gt; Cu &gt; Cd &gt; Zn &gt; Mn &gt; Co &gt; Mg &gt; Ni</td>
<td>(Shatirishvili and Zautashvili, 1981)</td>
</tr>
<tr>
<td>X</td>
<td>Cu &gt; Cd &gt; Mg &gt; Zn, Ni &gt; Co &gt; Mn</td>
<td>(Shatirishvili and Zautashvili, 1981)</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Ca &gt; Sr &gt; Ba</td>
<td>(Barrer and Townsend, 1976)</td>
</tr>
</tbody>
</table>

Table 4. A summary of ion exchange selectivity series from the literature. The ion-exchange is done at 25°C.
Zeolite A
5.61
0.19
29.1

DTPA
5.40
0.11
49.1

EDTA
4.96
0.12
41.0

Table 5. Economic calculation on zeolite A, DTPA and EDTA for chelation of manganese.

2.5 Zeolites in pulp bleaching

Zeolites in pulp bleaching are not used in the pulp and paper industry today. All the literature on the use of zeolites in pulp bleaching presented in the recent years deal with laboratory scale experiments except two field tests. Zeolites have been used on mechanical pulp (von Raven et al., 1989, von Raven et al., 1991, Leonhardt et al., 1992, Rivard et al., 1997) and DIP (deinked paper) (von Raven et al., 1989, Sain and Denault, 1996) but not on kraft pulp. The A type zeolite is the zeolite most extensively studied (von Raven et al., 1989, von Raven et al., 1991, Leonhardt et al., 1992, Sain and Denault, 1996, Rivard et al., 1997). Experiments with other aluminium silicates, such as the clay bentonite (von Raven et al., 1989) have also been performed. Advantages reported for zeolite based bleaching systems compared with systems based on sodium silicate and/or chelating agents are decreased hydrogen peroxide consumption and sodium hydroxide addition to the bleaching stage (von Raven et al., 1989, von Raven et al., 1991, Rivard et al., 1997). The decreased sodium hydroxide level contributes to decreased yellowing of the paper (von Raven et al., 1989, von Raven et al., 1991, Rivard et al., 1997), and decreased COD-levels (von Raven et al., 1989, von Raven et al., 1991, Sain and Denault, 1996, Rivard et al., 1997). For bleaching of deinked paper Sain
and Denault (1996) showed that an addition of zeolite A in the range one to four percent led to a decreased COD-level from 19.5 kg/ton to 16.2 kg/ton showing that the zeolite has an ability to take up small organic molecules. This has also been reported by other investigators (von Raven et al., 1989).

2.5.1 Additives

Different additives have been used when using zeolites in pulp bleaching. Von Raven et al. (1989, 1991) presented an activator/stabilizer system based on zeolite A activated with sodium carbonate or sodium hydrogen carbonate. One disadvantage with zeolites compared with chelating agents such as DTPA and EDTA is that the zeolite is in powder form with a diameter from a half to a few microns. Thus the zeolite can not diffuse into the fiber wall and chelate transition metals as well as the chelating agents can. Sodium citrate has been used as an additive by several investigators (Leonhardt et al., 1992, Sain and Denault, 1996, Rivard et al., 1997). It was reported that a combination of zeolite A with sodium citrate has a synergistic effect (Leonhardt et al., 1992) but little is known about the mechanism. One suggestion (Leonhardt et al., 1992, Sain and Denault, 1996) is that the citrate molecule has a greater complex forming constant than the pulp but smaller than that of the zeolite. The citrate which is water soluble can then diffuse into the fiber wall and chelate Mn ions and then diffuse out of the fibre wall and undergo an ion exchange with the zeolite. Another additive which has been proposed is polyphosphonic acid (Sain and Denault, 1996, Rivard et al., 1997). Zeolite A has also been used as a carrier for oxidation catalysts such as t-butyl hydroperoxide (t-BHP) (Sain and Denault, 1996) or a rhenium(VII) compound (Sain and Denault, 1996) in pulp bleaching.

2.5.2 How zeolites act in pulp bleaching

In the investigations published and patents filed for using zeolites in pulp bleaching it is not clear how zeolites act in this process. The process for using zeolites in pulp bleaching consists usually of a pretreatment stage were the chelation between the zeolite and the transition metal ions takes place. After this stage there could be a washing stage which normally consists of a press. In the washing stage the zeolite and the transition metals would be removed from the pulp before the bleaching stage. Sain and Denault (1996) used zeolite A in combination with
citrate and reported that they pressed the pulp to a consistency of 40 wt% before the bleaching stage but the levels of transition metals remaining in the pulp was not reported. Rivard et al. (1997) reported that they used a combination between zeolite A and polyphosphonic acid as a stabilizer which was directly added in the bleaching step. The question is then, does the zeolite work as a stabilizer and deactivate the transition metals in the bleaching liquor or is the effect that the transition metals are removed with the zeolite or is it a combination of both.

2.5.3 Process description of the pretreatment stage

There are few process parameters reported for the pretreatment stage in the investigations published and patents filed for using zeolites in pulp bleaching. In the pretreatment stage where the chelation between the zeolite and the transition metals takes place, there should be a certain pH-value, temperature, time and consistency to achieve optimum chelation of the transition metals.

2.5.3.1 pH in the pretreatment stage

Leonhardt et al. (1992) used pH 7.2 for zeolite A and when zeolite A is used in combination with citrate the pH is 7.2 (Leonhardt et al., 1992, Sain and Denault, 1996) in the pretreatment stage.

2.5.3.2 Temperature, time and consistency in the pretreatment stage

Temperatures reported in the pretreatment stage are 60°C (Rivard et al., 1997) and 70°C (Leonhardt et al., 1992). Rivard et al. (1997) treated the pulp in 30 minutes for 3 % consistency using zeolite A in combination with citrate.

2.5.4 The influence on the physical properties of paper when using zeolites in pulp bleaching.

Rivard et al. (1997) made an investigation on a thermo mechanical pulp (TMP) (70 % Spruce / 30 % Balsam) from a Canadian paper mill. The TMP was pretreated with 2 wt% (on dry pulp basis) of a Na-citrate modified Zeolite A containing 66 wt% Na-citrate. In a parallel
system, 0.5% of DTPA was used as a control. The pretreatment conditions were 3% pulp consistency, 60°C and a 30 min treatment time. In the bleaching system 3 wt% (on dry pulp basis) of a stabilizer which consists of zeolite A modified with polyphosphonic acid and two control systems was used. One control system used 3 wt% Na-silicate (41°Be) as a stabilizer and the other control system used 0.6% DTPMPA as a stabilizer which corresponds to the equivalent weight of the polyphosphonic acid adsorbed in the polyphosphonic modified zeolite A. The bleaching conditions were 12% consistency, 70°C for 2h. It is not clear from this investigation how the pulp is treated between the pretreatment stage and the bleaching stage.

<table>
<thead>
<tr>
<th>Nature of pretreatment</th>
<th>For bleaching comp. no 1 and 2.</th>
<th>For bleaching comp. no 3.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 wt % DTPA at 60°C for 30 minutes</td>
<td>2 wt% Na-citrate at 60°C for 30 minutes</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bleaching comp. no</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemicals added in the bleaching stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyphosphonic mod. zeolite, wt%</td>
</tr>
<tr>
<td>Na-silicate, wt%</td>
</tr>
<tr>
<td>DTMPA, wt%</td>
</tr>
<tr>
<td>Hydrogen peroxide, wt%</td>
</tr>
<tr>
<td>Sodium hydroxide, wt%</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>2.5*</td>
</tr>
<tr>
<td>3.0</td>
</tr>
<tr>
<td>0.6</td>
</tr>
<tr>
<td>2.5</td>
</tr>
<tr>
<td>2.0</td>
</tr>
<tr>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 6. The chemicals added in the pretreatment- and bleaching stage (Rivard et al., 1997).
As seen from table 6 and 7, the zeolite based system requires less sodium hydroxide and the peroxide consumption is lower for an equivalent brightness gain compared with the DTPA/Na-silicate and DTPA/DTPMPA-systems. The decrease in alkali charge for the zeolite based system also shows a decrease in the b value (see table. 7) indicating that the paper is less yellow for a given brightness. The zeolite based system also has very little influence on the mechanical properties. Rivard et al. (1997) also reported that the retention level was higher for the zeolite based system compared with the DTPA/Na-silicate and the DTPA/DTPMPA -systems. The zeolite based system also did not show any negative impact on a test with UV-radiation. The COD- level was also reduced to about 40 % compared with the DTPA/Na-silicate and the DTPA/DTPMPA -system.

2.5.5 Field tests.

There are two field tests reported, (von Raven et al., 1991) done at Werk Plattling and Werk Daschau. The zeolite system is called the Rawesol-system and is based on Patent DE 37 39 655 A1. There is no process description of the field tests or any information about what zeolite or what chelating agent that were used. The value of these tests, see table 8 and 9 is thus very limited.
<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>peroxide, wt%</td>
<td>0.52</td>
<td>0.83</td>
<td>1.29</td>
</tr>
<tr>
<td>Brightness, ISO-%</td>
<td>70.0</td>
<td>70.4</td>
<td>71.3</td>
</tr>
<tr>
<td>b-value (+/- 0.1)</td>
<td>11.7</td>
<td>11.3</td>
<td>11.0</td>
</tr>
<tr>
<td>Gain, ISO-%</td>
<td>10.7</td>
<td>11.1</td>
<td>11.4</td>
</tr>
<tr>
<td>b-change a</td>
<td>-0.1</td>
<td>-0.6</td>
<td>-0.8</td>
</tr>
<tr>
<td>Opacity, (+/- 0.1 %-ISO)</td>
<td>89.7</td>
<td>89.9</td>
<td>90.4</td>
</tr>
<tr>
<td>Scatt. coeff</td>
<td>62.0</td>
<td>-</td>
<td>60.1</td>
</tr>
<tr>
<td>Absorp. coeff.</td>
<td>0.93</td>
<td>-</td>
<td>1.02</td>
</tr>
<tr>
<td>Thickness</td>
<td>0.163</td>
<td>0.160</td>
<td>0.168</td>
</tr>
<tr>
<td>Burst index, (+/- 0.09 kPa. m²/g)</td>
<td>2.17</td>
<td>2.01</td>
<td>1.98</td>
</tr>
<tr>
<td>Tear index, (+/- 0.15 mN. m²/g)</td>
<td>5.7</td>
<td>5.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Breaking length, (+/- 0.12)</td>
<td>4.02</td>
<td>3.97</td>
<td>3.82</td>
</tr>
<tr>
<td>Breaking energy, (+/- 11 g. cm)</td>
<td>522</td>
<td>521</td>
<td>455</td>
</tr>
</tbody>
</table>

*a*-value is one of the CIE L*, a*, b* coordinates (CPPA standard method E-5P) and is a measurement of yellowness in the paper.

**Table 7.** The residual peroxide level, optical- and mechanical properties of the pulp. (Rivard et al., 1997).
<table>
<thead>
<tr>
<th>Bleaching chemicals, wt%</th>
<th>Standard addition of chemicals, wt%</th>
<th>Optimization 1, wt%</th>
<th>Optimization 2, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium silicate</td>
<td>1.75</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>0.44</td>
<td>0.00</td>
<td>0.30</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1.15</td>
<td>1.10</td>
<td>1.30</td>
</tr>
<tr>
<td>Rawesol</td>
<td>0.00</td>
<td>3.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Chelating agent</td>
<td>0.45</td>
<td>0.35</td>
<td>0.35</td>
</tr>
<tr>
<td>Brightness, (ISO-%)</td>
<td>70.3</td>
<td>69.5</td>
<td>70.1</td>
</tr>
<tr>
<td>Residual peroxide</td>
<td>15.0</td>
<td>17.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Table 8. Addition of chemicals and bleaching results from field tests at werk Plattling, 7-10/8 1989. (von Raven et al., 1991)
<table>
<thead>
<tr>
<th>Bleaching chemicals, wt%</th>
<th>Standard addition of chemicals, wt%</th>
<th>Optimization 1, wt%</th>
<th>Optimization 2, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium silicate</td>
<td>3.80</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>1.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Rawesol</td>
<td>0.00</td>
<td>3.00</td>
<td>2.5</td>
</tr>
<tr>
<td>Chelating agent</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Brightness, (ISO-%)</td>
<td>69.5</td>
<td>67.8</td>
<td>70.8</td>
</tr>
<tr>
<td>Residual peroxide</td>
<td>0.5</td>
<td>&gt; 10.0</td>
<td>3.5</td>
</tr>
</tbody>
</table>

*Table 9.* Addition of chemicals and bleaching results from field tests at werk Dachau, 30/7 - 1/8 1989. (von Raven et al., 1991)
3. Scope of this work

In the investigations of zeolites in pulp bleaching found in the literature, few details are presented regarding how the zeolites act in this process. It is not clear whether the zeolites act as stabilizers or if they act as chelating agents to facilitate removal of the transition metals from the pulp. There are no details given about the content of transition metals before or after the preatretment stage. Neither is there any information on how different types of zeolites act in pulp bleaching. There are also very few details provided on how different parameters such as the alkali charge or the charge of hydrogen peroxide influence the efficiency of the zeolites. In this work the aim was to:

1. Examine the fundamental chemical aspects of how zeolites affect the transition metal catalysed decomposition of hydrogen peroxide.

2. Examine how different zeolites act in pulp bleaching and how different process parameters influence the brightness gain and the residual peroxide.

3. Interpret the bleaching results in terms of chemical and catalytical effects of zeolite addition.
4. Summary of the work

The experimental work forming the basis for this thesis can be divided into two parts. In the first part, the effects of various zeolites on the manganese catalysed decomposition of hydrogen peroxide were studied in a simple model system. The purpose of this work was to obtain a fundamental understanding of the zeolite-Mn-peroxide system but also to facilitate the selection of zeolites for further studies in actual bleaching experiments. These bleaching experiments, using both mechanical and kraft pulp constituted the second part of the work. The work has been presented in three scientific articles. In the first of these (paper I), the results of the fundamental study in the model system are presented and discussed. The evaluation of the use of zeolites in bleaching process is presented in paper II whereas paper III can be regarded as an attempt to link the two experimental parts together. Below, a summary of the two experimental parts is given with reference to the three papers. Some experimental results not included in the articles are also discussed in this section.

4.1 Fundamental studies of the system zeolite-Mn-peroxide

The investigation (paper I) of how zeolites influence manganese catalysed decomposition of hydrogen peroxide was done in a simple model system containing a hydrogen peroxide solution and manganese. In an industrial pulp bleaching application the situation is further complicated by the presence of the pulp, other additives, dissolved organic substances and various cations present in the bleaching liquor. The results from this simple model system are rather confusing and it is difficult to draw any general conclusions. It seems that a given zeolite can give both an inhibiting and a promoting effect on the manganese catalysed decomposition of hydrogen peroxide depending on the pH and the ratio between the zeolite and the manganese present in the solution. For instance Mordenite 10 A in a twofold excess showed an inhibiting effect at pH 10.8 whereas the other zeolites tested gave no or little effects on the reaction rate at this pH (see table 3, paper I). Zeolite A which is the most extensively studied zeolite for use in bleaching (von Raven et al., 1989, von Raven et al., 1991, Leonhardt et al., 1992, Sain and Denault, 1996, Rivard et al., 1997) showed promotive effects at pH 9.9 in the stochiometric ratios from 2 to 5 (See table 3, paper I). At pH 9.0 when the stochiometric ratios is between 2 to 3, zeolite A promoted the decomposition of hydrogen peroxide. But when the stochiometric ratio reached 4 the zeolite started to show an inhibiting
effect and at a ratio of 5 the inhibition of the decomposition is nearly total (see figure 1 and 5, paper I). Zeolite A have three different ion exchange sites SI, SII and SIII (Förster and Witten (1988). Preferential exchange into specific sites and specific catalytic properties of ions bonded in these sites could possibly explain the trends observed.

Advantages reported with zeolite based bleaching systems compared with systems based on sodium silicate and/or chelating agents is decreased addition of sodium hydroxide to the bleaching stage (von Raven et al., 1989, von Raven et al., 1991, Rivard et al., 1997) to achieve nearly the same brightness. One explanation of how the zeolite A acts in pulp bleaching could be that the zeolite deactivates manganese at lower pH, around 9.0 or lower.

4.2 Use of zeolites as additives in the bleaching of mechanical pulp

The following zeolites were investigated; zeolite A, P, Y and mordenite 10 A, for bleaching of a TMP pulp (see paper II). The aim with this investigation was to determine how different factors such as the bleaching pH, consistency, the type and the charge of the zeolite influence the brightness and residual peroxide level. A comparison was also made for the bleaching efficiency between zeolites and the conventional chelating agents EDTA and DTPA.

Zeolite A was used to investigate the effect of the zeolite charge and was varied in the range 0-4 wt% (on dry pulp basis). The brightness was increased to a zeolite charge of approximately 2 wt%. The residual peroxide level showed a continuous increase with increasing amount of zeolite added within the range studied, with a slightly tendency for the curve to level out at higher zeolite charges.

An addition of 4 wt% zeolite was used to investigate the alkali charge which was varied in the range from 0.0 to 2.0 wt% (on dry pulp basis). As expected the residual peroxide level decrease with an increased alkali level. This decrease was, however, significantly less pronounced for the series performed with the addition of zeolite A. The optimal ISO-brightness was around 68 for the sample containing zeolite A and for the sample without zeolite addition it was about 65.5%.

The consistency in the bleaching stage was investigated for a sample containing 4 wt% zeolite A. The ISO-brightness increased with 4 % when moving from 3% to 10 % consistency and the residual peroxide level was only slightly decreased. Higher consistencies were not investigated because the equipment was not useful for that purpose.
An addition of 4 wt% of different zeolites showed that the A and P type zeolites gave a positive bleaching result both regarding the residual peroxide level and ISO-brightness. Mordenite 10 A and zeolite Y had no positive or nearly no influence of the bleaching result. At the lowest alkali charge (0.4 wt%) tested, zeolite Y gave a decrease in the residual peroxide, indicating that this zeolite could have a promoting effect on the decomposition of hydrogen peroxide.

Addition of 0.2 wt% of the chelating agents DTPA and EDTA resulted an improvement of the bleaching results compared with the best bleaching results achieved with zeolite A. The effect was more notable at higher alkali charges, but at lower alkali charge the results from the bleaching with zeolite A were closer to the results reached with the chelating agents EDTA and DTPA.

4.3 Use of zeolites as additives in the bleaching of chemical pulp

A charge of 4 wt% zeolite A was used on a chemical (kraft) pulp at three different alkali charges; 0.4, 1.0 and 1.6 wt% (see paper II). At the lowest alkali charge investigated, a modest positive effect of zeolite addition was observed as signified by a higher residual peroxide content in the bleaching liquor. The brightness obtained at these conditions was, however, slightly lower than that reached in the absence of zeolite. When increasing the alkali charge the difference between the bleaching results in the presence of zeolite A compared with no zeolite addition was even more pronounced and at a charge of 1.6 wt % the difference obtained in the presence of zeolite was almost 10 % lower. These results as well as other results obtained for bleaching of chemical pulps in our laboratory in the presence of zeolites indicated that the zeolites in most instances not have a positive effect on the bleaching performance of the peroxide. An explanation could be the fact that, at high pH levels, the zeolite appears to promote rather than inhibit the catalytic action of the manganese the presence of which is believed to be the primary cause of peroxide decomposition (Paper I). One conclusion is that zeolite A is not suitable for bleaching of kraft pulp because the pH is usually high (pH > 10.0) (Troughton et al., 1994, Desprez et al., 1993).
4.4 How different zeolites act as stabilizers in pulp bleaching

The aim with this investigation was to investigate whether the zeolites act as stabilizers in the bleaching stage. There is no washing (press) stage between the pretreatment stage and the bleaching stage as for the bleaching experiments represented in paper II. In these bleaching experiments, there is consequently no reduction of transition metals or zeolite content between the pretreatment and the bleaching stage. The zeolites used in this investigation were: zeolite A, P, X, Y and mordenite 10 A and an addition of 0.2 wt% DTPA was used for comparision. As can seen from figure 4 and 5 zeolites A and P had a positive impact both on the residual peroxide level and the ISO-brightness, zeolite X and Y give a decrease in both these parameter. Those latter zeolites appears to give a promoting effect on the decomposition of hydrogen peroxide. Mordenite 10 A on the other hand shows no effect on the residual peroxide level and no or a little positive effect in brightness if 4 % of the zeolite is added. This investigation shows that some zeolites has a stabilizing effect on the hydrogen peroxide in the bleaching stage while other ones have a promoting effect. A comparision with DTPA at the conditions used in this investigation, shows that it takes about of 4 wt% zeolite A to get the same performance as 0.2 wt% DTPA.
Figure 4. A comparison of how different zeolites and DTPA act as stabilizers in pulp bleaching. Effect on brightness when bleaching a TMP pulp at 70°C, 3% consistency for 3h with a solution initially containing 2 wt% hydrogen peroxide and 1.2 wt% sodium hydroxide.
Figure 5. A comparison of how different zeolites and DTPA act as stabilizers in pulp bleaching. Effect on the residual peroxide level when bleaching a TMP pulp at 70°C, 3% consistency for 3h with a solution initially containing 2 wt% hydrogen peroxide and 1.2 wt% sodium hydroxide.
4.5 Investigation of the pH-drop.

The pH-drop and the pH during bleaching was measured on the TMP pulp which was used in the bleaching experiments in Paper II. As can bee seen from figure 6, the pH declines very rapidly under the first 20 minutes in the bleaching stage and after that slowly during the rest of the bleaching period. Except for the initial period the pH is close to or below 9 during the bleaching process.

![Graph of pH vs time](image)

Figure 6. Investigation of the pH when bleaching a TMP pulp (pretreated with 4 wt% zeolite A on weight basis) at 70°C, 10 % consistency for 3h with a solution initially containing 2 wt% hydrogen peroxide and 1.0 wt% sodium hydroxide.

4.6 Investigation the zeolite contribution to the brightness when used as a filler

The zeolite could act as a filler in the pulp and contribute to the brightness because it has a high brightness (see table 1). In order to investigate how much brightness gain that is derived from the zeolite and how much is due to the higher residual peroxide level in the bleaching liquor, the following experiments were done. A zeolite slurry was carefully mixed with a stirrer rod into a the pulp. The pulp is then pressed to a sheet and dried after which the brightness was measured. This is just a simple experiment and the effect must be further
investigated by other methods, but the results presented in figure 7 shows that the zeolite does not contribute to the brightness as a filler.

Figure 7. Investigation of how zeolites acts as fillers in the pulp.
5. Conclusions

In this thesis a simple model of the system zeolite-peroxide-manganese in the bleaching stage was initially used (paper I). The model system is very simple considering all the factors which influence the system in the bleaching stage like; the ion exchange sites in the pulp, the ion matrix and organic substances. Despite the simplicity of the model system, the chemistry turned out to be very complex with different zeolite showing both inhibiting and promoting effects on the catalytic decomposition of hydrogen peroxide depending on the pH and the stochiometric ratio between the zeolite and manganese. Certain zeolites such as mordenite 10 A show an inhibitive effect on the decomposition of hydrogen peroxide at high pH values and a promotive effect at lower values (pH 9-10). Zeolite A and zeolite P showed an inhibitive effect at lower pH values when added in great excess. Zeolite A on the other hand showed promotive effects on the decomposition rate at pH 9.9 even if an excess was used. Zeolite A which is the most commonly investigated zeolite had a remarkable inhibiting effect at pH 9.0 when the zeolite was added in great excess (stochiometric ratio zeolite : Mn, 5:1). At lower stochiometric ratios (zeolite A : Mn, < 3:1) the zeolite showed a promotive effect on the decomposition rate. One possible explanation as to why the zeolite could show both inhibiting and promoting effects on the catalytic decomposition on hydrogen peroxide depending on the stochiometric ratio could be that the zeolite has different ion exchange sites. For instance zeolite A contains three different sites SI, STI and SM. Preferential exchange into specific sites and specific catalytic properties of ions bonded in these sites could possibly explain the trends observed.

Disadvantages of the zeolite when chelating transition metal ions is that the zeolite is in powder form with a size from a half to some microns and that the zeolites usually have a high selectivity for chelating calcium ions. Because the zeolite is in powder form it is not so effective as the chelating agent and cannot diffuse into and out from the fibers to chelate ions. Different investigators have used citrate as an additive to get a better transport of ions from the pulp to the zeolite. The ion matrix in the pulp contains high amounts of calcium, so a lot of the ion-exchange capacity could be lost, chelating calcium ions.

One possible explanation for how zeolite A, the most commonly investigated zeolite, act in pulp bleaching could be that it inhibits the catalytic decomposition at pH values below or around 9.0. The pH during the bleaching was investigated on the TMP pulp used in the
bleaching experiments as was found to be below 9 for about 90% of the bleaching period for the bleaching conditions which gave the best bleaching results with zeolite A.

A number of bleaching experiments was done on a chemical (TMP) pulp to see if different zeolites act as stabilizers in pulp bleaching. In these experiments the pulp was treated in a pretreatment stage and the bleaching chemicals are added in this stage, so there was no reduction of transition metals or added zeolite between the pretreatment and bleaching stage. Zeolite A and P acted as stabilizers and had a positive impact both on the residual hydrogen and the brightness, zeolite X and Y gave an decrease in both these parameters whereas mordenite 10 A had no or little influence. It seems like zeolite X and Y have a promotive effect on the decomposition of hydrogen peroxide.

A comparison with DTPA at the condition used showed that it takes about 4 wt% zeolite A to achieve the same performance as 0.2 wt% DTPA.

A comparison between zeolites and the chelating agents EDTA and DTPA was done on a mechanical (TMP) pulp and a chemical pulp in conventional bleaching experiments. In those experiments there was a washing (press) stage between the pretreatment and the bleaching stage and in the washing stage there is a reduction of transition metals, chelating agents and added zeolite in the pulp. An addition of 4 wt% zeolite at three different alkali charges 0.4, 1.0 and 1.2 wt% was used in these experiments. In bleaching of the mechanical pulp the zeolites A and P had a positive effect both on the residual peroxide level and the ISO-brightness. Mordenite 10 A and zeolite Y had little or no effect on the bleaching result, and at the lowest alkali charge (0.4 wt%) zeolite Y even showed a promoting effect on the decomposition of hydrogen peroxide. An increase of the consistency from 3 to 10% gave an increase in ISO-brightness with about 4% with little reduction of the residual peroxide level for zeolite A. One way to increase the effect of an addition of zeolite A could be to increase the consistency to 20% or higher.

At all conditions an addition of 0.2 wt% of the chelating agents EDTA and DTPA resulted in an improvement of the bleaching results as good as or much better than the best bleaching results achieved with an addition of 4 wt% zeolite A.

4 wt% zeolite A was used on a chemical (kraft) pulp. At the lowest alkali charge investigated a modest positive effect of zeolite addition obtained as signified by a higher residual peroxide level. The brightness was however slightly lower for the zeolite containing sample. The effect of lower brightness for the zeolite containing was even more notable at higher alkali charge and at 1.6 wt% the difference was nearly 10%. High pH in the bleaching liquor is one explanation why zeolite A has a negative impact on bleaching of chemical pulps.
The amount of zeolite (zeolite A) required to give a substantial effect in the bleaching of mechanical pulp was about 4 wt% (on dry pulp). Using the content of Mn as a basis, this was approximately twenty times as much as the amount needed to obtain a maximal effect in the model system.

This investigation showed that the effect of increased brightness when zeolite A was used in pulp bleaching depends on higher residual peroxide level in the bleaching liquor and that the zeolite did not contribute to the brightness, acting as a filler.

This investigation showed that zeolite A and P which have the highest ion exchange capacity of the known zeolites and are commercially used in detergents, showed the best bleaching result on mechanical pulps. On chemical pulps zeolite A was used and had a negative influence on the bleaching result probably due to the high pH in the bleaching liquor.

The methods and zeolites used in this investigation showed that the efficiency of the zeolites is not enough to substitute the chelating agents EDTA and DTPA in bleaching of mechanical pulps.
6. Further Developments

(1) The work on bleaching of mechanical pulps should proceed with zeolite A and P or some other zeolite which is not tested in this investigation. Preferably with a zeolite which has a higher selectivity towards transition metals than for calcium or magnesium ions. A zeolite with those characteristics has not been found in this investigation.

(2) The zeolite itself does not show enough efficiency according to this investigation. The use of a complementary chelating agent (preferably biodegradable) and/or a buffer may help in order to achieve a better performance with the zeolite.

(3) An improvement of the ion exchange in the chelating stage could further improve the bleaching result with the zeolite. This investigation has shown that maybe as little as 1/20 of the zeolites (zeolite A) capacity is used.

(4) Other ion exchangers such as, clays or aluminosilicate compound should be investigated as alternatives to zeolites.
7. Acknowledgments

First of all I would like to express my sincere gratitude to my supervisor, Professor Johan Sterte for his helpful advice, optimism, inspiration and encouragement during this work. I would also like to thank my friends and colleges in the division of Chemical Technology; associate Professor Brian Schoeman, Mr. Jonas Hedlund, Ms. Vania Engström, Mr. Olle Niemi, Dr. Elena Babouchkina, Ms. Guangy Zhang and our secretary Ingrid Granberg for their helpfulness and companionship during this work.

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Effects of Zeolite Addition on the Manganese Catalysed Decomposition of Hydrogen Peroxide

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Effects of Zeolite Addition on the Manganese Catalyzed Decomposition of Hydrogen Peroxide

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Abstract. Manganese catalysed decomposition of hydrogen peroxide in the presence of various zeolites was investigated at different pH values, Mn concentrations and zeolite:Mn ratios. Depending upon the level of these parameters the zeolites studied displayed both catalytic and inhibitive effects on the rate of decomposition. At a high pH (10.8) Mordenite 10A in a twofold excess on an ion-exchange capacity basis acted as an inhibitor whereas the other zeolites had little or no effect on the reaction rate. At a lower pH (9.0) zeolite A when added in large excess resulted in a remarkable inhibitive effect whereas the same zeolite resulted in a promotion of the catalytic action of manganese at an intermediate pH (9.9). The complex catalytic nature of the zeolite-peroxide-Mn systems is discussed.

Introduction

Due to environmental considerations, most manufacturers of pulp have phased out the use of elementary chlorine in their bleaching processes. In order to minimize the amount of chlorinated organic substance in the bleaching effluents or to completely avoid the formation of such substances, processes have been developed using bleaching agents such as chlorine dioxide, ozone and hydrogen peroxide. Bleaching without the use of chlorine containing chemicals, usually termed TCF (totally chlorine free)-bleaching, generally involves a sequence of operations including one or more treatments with alkaline hydrogen peroxide. A problem associated with the use of hydrogen peroxide in this application is that some transition metal substances are very efficient in catalyzing the decomposition of the peroxide into water and oxygen thus preventing effective use of the peroxide for bleaching of the pulp. The pulp contains trace amounts of transition metal ions (Mn, Fe and Cu) introduced mainly with the raw material. Among these transition metals manganese has the most deleterious effect on peroxide stability, partly due to the fact that the level of manganese is higher than that of the other cations and, partly because the copper and iron ions are stronger complexed with the wood components [1]. Both chemical and mechanical pulp generally contain about 50-100 ppm calculated on dry pulp basis, the amount depending upon the geological conditions at the growth place of the trees used as raw material.
Presently, the transition metal problem is handled by the use of a chelating step (Q-step) prior to the peroxide bleaching (P-step). In the Q-step a chelating agent such as EDTA or DTPA is used for chelating the transition metal ions which are then removed in a subsequent washing step. From a processing point of view this works quite satisfactory although the utilization of hydrogen peroxide is still limited by decomposition due to remaining transition metals. The chelating agents used are, however, questionable from an environmental standpoint. They are known to be non-biodegradable or only very slowly degraded in water [2]. Concern has arisen that they, due to their high binding constants with heavy metals ions, has the potential to solubilize metals from solid particles (i.e., sediments or colloidal soil constituents) to the dissolved aqueous state [3,4]. This has resulted in increased restrictions of the industrial use of chelating agents and created a strong incentive for the pulp and paper industry to find alternative materials or processes through which the metal problem can be handled.

One alternative which has been proposed in the literature is to substitute the chelating agents with zeolites. This is not surprising since zeolites are known to have a large cation-exchange capacity and unique selectivity properties connected with their pore structure, a fact that is utilized in other applications requiring selective removal of cations from aqueous solutions. A number of patent applications [5,6] and technical publications [7-9] dealing with the use of zeolites for prevention of hydrogen peroxide decomposition in pulp bleaching have been published in the last few years. This work which primarily has been focused upon the use of zeolite A as an additive in the hydrogen peroxide bleaching of mechanical pulp indicates that the zeolite alone or in combination with other additives results in an improved bleaching efficiency as signified by an increased brightness of the pulp and a lowered consumption of hydrogen peroxide. For the zeolite to give this positive effect it is not sufficient that it selectively takes up the manganese ions from the pulp matrix solution. As the zeolite, being a solid material, can not be effectively removed from the pulp after the addition, the manganese will remain in the pulp, bonded in the zeolite structure during the bleaching process. It is therefore a further requirement that the manganese exchanged zeolite is not an active catalyst for the decomposition of hydrogen peroxide. It should be noted that organic chelating agents such as EDTA and DTPA currently used merely serves as a means to remove transition metals and are separated from the pulp in a washing procedure prior to the P-step. If present during the bleaching (with peroxide stabilized with magnesium/silicate combination), DTPA slightly inhibits the catalytic effect of manganese and copper ions but promotes that of iron [10].

All work concerning the use of zeolites in this area so far reported in the literature is of a very technically applied nature. No reports of systematic investigations involving different types of zeolites or attempting to explain the fundamental chemical mechanisms responsible for the positive results obtained have appeared. The objective of the present study was to investigate the effects of a series of zeolites on the catalytic decomposition of hydrogen peroxide using a simple model system. A further objective was to generate data and define criteria for selection of
zeolite types to be studied in further experiments with more complex model systems and industrial pulp samples.

**Experimental**

**Materials**

The water used in all experiments was double distilled and all chemicals were of reagent grade. The hydrogen peroxide used was PERDROGEN® (30 wt% H₂O₂, Riedel de Haën) with a metal content specified to be: Mn < 0.000001 %, Cu < 0.000001 %, Fe < 0.000005 % and Mg < 0.000005 %. The manganese stock solution was made from MnSO₄·H₂O (Riedel de Haën) with the following specification: Cu < 0.005 %, Fe < 0.001 % and Mg < 0.005 %. A stock solution containing 1000 ppm Mn was prepared by dissolution of the manganese salt in distilled water. Sodium Hydroxide (Riedel de Haën, Cu < 0.001% and Fe < 0.001 %) and sulfuric acid (Riedel de Haën, Mn < 0.000005 %, Fe < 0.00001 %, Cu < 0.000001 % and Mg < 0.000005 %) were used for pH-adjustment.

The zeolites used in this study were: zeolite A (Wessalith P, Degussa AG), zeolite P (Crossfield), Mordenite 10A (Akzo Nobel AB), zeolite Y (Akzo Nobel AB) and zeolite X. Zeolite X was synthesized in our laboratory [11]. Chemical compositions of the zeolites are given in Table 1.

**Catalytic decomposition of hydrogen peroxide**

The catalytic decomposition of hydrogen peroxide was investigated by the following experimental set-up consisting of a 2 l glass beaker placed on a heating plate with a magnetic stirrer and equipped with a temperature control unit. The temperature was controlled within +/- 1°C. The pH was measured with a Methrom 691 pH meter equipped with a Methrom 6.1110.100 electrode and connected to a temperature compensating electrode.

The catalytic decomposition of hydrogen peroxide by Mn was investigated using the following experimental procedure:

Solutions of Mn with desired concentrations in the range of 0.25-4 ppm and with a pH OF 5-6 were prepared by dilution of the required volume of the stock solution with an amount of water calculated to give a final volume of 1500 ml in the actual experiment. The solution was heated to 70°C. The amount of zeolite calculated to have a total ion-exchange capacity corresponding to an excess of 2:1-5:1 with respect to Mn⁺⁺, was placed in a small polyethylene beaker. Distilled water (20 ml) was then added to the zeolite and the pH was adjusted to a value in the range 5-6. The zeolite suspension was added to the glass reactor under stirring and the zeolite was left in contact with the solution for 30 min. Without removal of the zeolite, the pH was then adjusted to a predetermined value in the range 9.0-10.8 by addition of sodium hydroxide. Hydrogen peroxide (50 ml, 0.30 M, adjusted to
the pH selected) corresponding to an initial concentration of 0.010 M in the experiment was then added under stirring. Samples of 20 ml were withdrawn from the reactor and analyzed for their content of H₂O₂.

**Analysis of hydrogen peroxide**

The H₂O₂ content in the samples was analysed using iodometric titration [12]. Directly upon withdrawal, the samples was added to a solution made up from 70 ml 4.0 M H₂SO₄, 10 ml 1.0 wt% KI and 5 ml of a 0.20 wt% starch solution in order to stop the reaction.

**Results and discussion**

**Manganese catalysed decomposition of hydrogen peroxide**

In order to assess the catalytic effects of manganese on the decomposition of hydrogen peroxide in the absence of zeolites and thus to provide references for experiments with various zeolites present, a series of experiments were made varying the pH and the Mn content of the solutions.

![Figure 1. Catalytic decomposition of hydrogen peroxide in a solution containing 1.0 ppm Mn at pH 9.0, 9.9 and 10.8.](image)
Figure 1 shows the conversion of H$_2$O$_2$ as a function of time at various pH values in the range 9.0-10.8 in solutions containing 1 ppm Mn. As seen in this figure, the presence of Mn catalyses the decomposition of H$_2$O$_2$ most effectively at the highest pH studied, i.e. pH 10.8. The rate of decomposition is considerably lower at pH 9.0 and lowest at pH 9.9, indicating the existence of a pH dependent minimum of the reaction rate. A similar, but considerable less pronounced minimum was observed by Colodette et al. [13], when studying the decomposition of H$_2$O$_2$ in the presence of Mn. In their study, somewhat different conditions were used which may explain the discrepancy between their observations and the ones reported here.

Figure 2 shows first order reaction plots obtained using the data presented in figure 1. A good linear correlation is obtained for all cases indicating that the assumption of first order kinetics of the decomposition of H$_2$O$_2$ at a constant metals content in the solution is valid. This observation is also in good agreement with previous studies proposing that H$_2$O$_2$ is heterogeneously decomposed on the active sites of manganese oxides, and that this reaction is first order [14,15]. Figure 3 shows the conversion of H$_2$O$_2$ as a function of time at pH 10.8 when adding different amounts of Mn. The activity observed in the absence of added Mn is most likely mainly due to the presence of trace amounts of metals in the sodium hydroxide used for pH regulation. It has been shown that even if extensive measures are taken to purify the hydroxide, a sufficient amount of transition metals are still present to yield an observable catalytic effect [16]. The addition of 0.25 ppm Mn...
Mn results in a marked increase in the rate of decomposition of H₂O₂, a rate which, as expected, increases further upon addition of 1 and 4 ppm Mn, respectively. The rate constants for Mn-catalysed decomposition of H₂O₂, calculated assuming first order kinetics are given in table 2. The observed increase in the rate constants with increasing Mn-content in the solution is not directly proportional to this Mn-content. Different mechanistic explanations for the Mn-catalysed decomposition of H₂O₂ have been proposed in the literature involving both homogeneous processes catalysed by transition metal cations and heterogeneous catalysis by finely dispersed colloidal transition metal oxides or hydroxides [13]. As the solubility of Mn in the pH range studied in this work is extremely low, the existence of any significant amounts of manganese cations in solution appears unlikely. Neither does the HMnO₄⁻-ions proposed to participate in the catalytic decomposition of H₂O₂ in highly alkaline solutions [17] appear to be a possible catalyst at the considerably less alkaline conditions used in the present study. The catalytic action observed upon addition of Mn is therefore most likely due to colloidal manganese hydroxide or hydrated manganese oxide particles. If so, and

Figure 3. Catalytic decomposition of hydrogen peroxide at pH 10.8 in solutions containing 0, 0.25, 1.0 and 4.0 ppm Mn.
Table 1. Characterization of zeolite samples used

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Structural formulaa</th>
<th>CECb (meq/g)</th>
<th>water cont.c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2 SiO₂ Al₂O₃ Na₂O</td>
<td>7.0</td>
<td>20.0</td>
</tr>
<tr>
<td>P</td>
<td>2 SiO₂ Al₂O₃ Na₂O</td>
<td>7.0</td>
<td>13.8</td>
</tr>
<tr>
<td>X</td>
<td>2.5 SiO₂ Al₂O₃ Na₂O</td>
<td>6.4</td>
<td>16.8</td>
</tr>
<tr>
<td>Y</td>
<td>5.3 SiO₂ Al₂O₃ Na₂O</td>
<td>4.1</td>
<td>25.2</td>
</tr>
<tr>
<td>M 10A</td>
<td>13 SiO₂ Al₂O₃ Na₂O</td>
<td>2.1</td>
<td>10.6</td>
</tr>
</tbody>
</table>

aCalculated from elemental analyses provided by the manufacturers.
bCalculated for dehydrated zeolites from structural formulae.
cBased on weight loss upon calcining at 400°C in air for 4 h

Table 2. Catalytic decomposition of hydrogen peroxide in the absence of zeolites

<table>
<thead>
<tr>
<th>C_{Mn} (ppm)</th>
<th>pH</th>
<th>k (min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.0</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>0</td>
<td>9.9</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>0</td>
<td>10.8</td>
<td>&lt;0.000</td>
</tr>
<tr>
<td>1.0</td>
<td>9.0</td>
<td>0.035</td>
</tr>
<tr>
<td>1.0</td>
<td>9.9</td>
<td>0.025</td>
</tr>
<tr>
<td>1.0</td>
<td>10.8</td>
<td>0.136</td>
</tr>
<tr>
<td>0.25</td>
<td>10.8</td>
<td>0.058</td>
</tr>
<tr>
<td>4.0</td>
<td>10.8</td>
<td>0.298</td>
</tr>
</tbody>
</table>

assuming that these colloidal species are chemically identical, the reaction rate should be proportional to the total surface area of the catalytic colloids rather than
to the concentration of Mn in the solution. The differences observed in the rate constants when increasing the amount of Mn added from 0.25 to 4 ppm could thus reflect an increase in the total surface area of the active phase accompanied with a slight decrease in the specific surface area (m²/g) of the particles formed.

**Effects of zeolite addition**

In order to establish the effects of addition of various zeolites on the decomposition of H₂O₂ in the presence of Mn a series of experiments was performed using a calculated twofold excess of zeolite (on a total ion-exchange capacity basis), a Mn-content of 1 ppm and a pH of 10.8. This pH was chosen as an initial pH in the range 10-11 is commonly used in the bleaching of mechanical pulp.

Figure 4 shows the rate of decomposition of H₂O₂ when adding different types of zeolites. As can be seen in this figure, the only zeolite type significantly affecting the decomposition rate as these conditions is Mordenite 10A, addition of which resulted in a strong inhibition of the catalytic effect of Mn. As mentioned above, most of the previous work in this area published in the literature concern the use of zeolite A as the preferred zeolite additive [5-9]. It was therefore somewhat surprising that addition of this zeolite at the given conditions did not show any inhibition effects whatsoever. On the basis of the results obtained, Mordenite 10A was chosen for further studies. Due to the particular interest focused on zeolite A in the literature, this zeolite was also selected for a more thorough investigation.

![Conversion vs. Time](image)

**Figure 4.** Effects of zeolite addition (zeolite:Mn = 2:1 on a CEC-basis) on the catalytic decomposition of hydrogen peroxide at pH 10.8 in a solution containing 1.0 ppm Mn.
Mordenite 10 A

In order to further evaluate the effects of mordenite addition on the catalytic decomposition of hydrogen peroxide one series of experiments was performed using the same conditions as those used above but at three different levels of the Mn-content. The results of these experiments are presented in the form of first order rate constants in Table 3. A comparison of the rate constants obtained at pH 10.8 in the presence of mordenite with those calculated for the reaction in the absence of the zeolite (given in Table 2) reveals that the former rate is approximately 40% of the latter one. Within the concentration range studied the inhibition effect of the mordenite thus appears to be essentially independent upon the Mn concentration. A series of experiments was also performed using the same conditions but varying the initial pH values in the range 9.0-10.8. The first order rate constants obtained in these experiments are also reported in Table 3. A comparison with the corresponding values obtained at identical conditions but in the absence of zeolite (see Table 2) results in a somewhat confusing picture.

Table 3. Catalytic decomposition of hydrogen peroxide in the presence of zeolites

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>zeol:Mn&lt;sup&gt;a&lt;/sup&gt;</th>
<th>C&lt;sub&gt;Mn&lt;/sub&gt; (ppm)</th>
<th>pH</th>
<th>k (min&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mord.</td>
<td>2:1</td>
<td>1.0</td>
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<tr>
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<td>5:1</td>
<td>1.0</td>
<td>10.8</td>
<td>0.113</td>
</tr>
</tbody>
</table>

<sup>a</sup>Amount of zeolite used in relation to the amount of Mn<sup>2+</sup> present in the solution based on the ion-exchange capacity of the zeolite.
While addition of mordenite in a 2:1 excess at pH 10.8 results in a significant inhibition of the Mn-catalysed decomposition of H₂O₂, the effect at the lower pH values studies is a promotion of this decomposition. In this lower pH range, Mn incorporated into the mordenite structure thus appears to be more active catalyst for this reaction than the colloids presumably responsible for the catalytic action when no zeolite is added.

Zeolite A

In order to further investigate the effects of addition of zeolite A on the Mn-catalysed decomposition of H₂O₂, the effects of pH was investigated, using the same basic conditions as those given above. The first order rate constants calculated for the decomposition at different pH values in the range 9.0-10.8 are given in Table 3. In contrast to the corresponding values obtained for the reaction in the absence of zeolite, the rates observed show little dependence upon pH. At all pH levels studied, the rate of decomposition is however, faster in the presence of zeolite A in an amount corresponding to a twofold excess on the basis of the total ion-exchange capacity than in the absence of zeolite.

A number of experiments were performed at pH 9.0 using the same conditions as above but adding increasing amounts of zeolite A to the solutions. The results of these experiments are shown in Figure 5. As seen, the effects of van increased zeolite charge were dramatic. An addition of a twofold excess (zeolite:Mn) resulted

Figure 5. Effects of the amount of zeolite A added on the catalytic decomposition of hydrogen peroxide at pH 9.0 in a solution containing 1.0 ppm Mn.
in a complete decomposition of the H$_2$O$_2$ in about 30 min whereas less than 20% of
the peroxide was decomposed after 100 min when the zeolite charge was
increased to a fivefold excess.

Using a fivefold excess of zeolite A but increasing the pH to 9.9 and 10.8,
respectively, a catalytic rather than an inhibitive effect was again obtained for
zeolite A addition, see Table 3.

Discussion

The results presented above show that the effects of zeolite addition on the Mn
catalysed decomposition of H$_2$O$_2$ are very complex. Zeolite addition can affect this
decomposition both by inhibiting the catalytic effect and by enhancing it,
depending upon the reaction conditions used, the type and the amount of zeolite
added. It is difficult to see any general trends in the results obtained, essentially all
parameters investigated affect the catalytic decomposition of the H$_2$O$_2$ but not in a
manner allowing for simple mechanistic explanations connected e.g. with the ion-
exchange capacity of the zeolite. One should, however, keep in mind that while the
catalytic decomposition of H$_2$O$_2$ in the presence of Mn itself is rather complicated
and has been the subject of a number of recent investigations (see eg. [14,15]), the
addition of a zeolite to this system makes it even more complex by introducing a
number of possible chemical events that may contribute to the catalytic behaviour
of the system.

In the experiments Mn was added in the form of Mn$^{2+}$ (manganese sulfate). At
alkaline conditions and with dissolved oxygen available, Mn$^{2+}$ will be oxidized,
mainly to Mn(IV) and a precipitate believed to consist of hydrous manganese
dioxide will form [13]. The precipitation is visually observable by the naked eye
even at Mn contents as low as 1 ppm. The precipitated colloid which most likely is
the active catalyst for the decomposition of H$_2$O$_2$ is probably non-stoichiometric with
the main part of the Mn in the +IV state and the remaining part in the +III state[15].
Despite the fact that zeolites have been extensively used as ion-exchangers, the
literature data on the ion-exchange selectivity of various zeolites for Mn$^{2+}$ is very
scarce. By preliminary experiments in our laboratory investigating the exchange of
Mn into various zeolites in the sodium form (not presented here) we found that
introduction of zeolite A or mordenite 10 A in an excess into a system containing
Mn$^{2+}$ at a pH of 5-6 results in the incorporation of the main fraction of the Mn into
the ion-exchange sites of the zeolite. From a catalysis point of view, the situation is
complicated by the fact that zeolites contain a number of structurally different ion-
exchange sites, sites which may have different preferences for different cations. In
catalytic processes, different active sites connected with these ion-exchange
sites, are believed to be responsible for distinct catalytic transformations. The
selectivity of these catalytic sites may vary with the type of cation.

Raising the pH of the solution from 5-6 where the ion-exchange takes place to the
initial pH of the reaction and introducing H$_2$O$_2$ may further affect the chemistry of
the zeolite containing system. In analogy with the zeolite free system, the Mn$^{2+}$ ions
could be oxidized to a higher valency and a solid precipitate could form. In a
zeolite containing system, this precipitate would be likely to form in the pore system or on the external surface of the zeolite crystals. The presence of the zeolite acting as a carrier for the catalytic phase would probably influence the dispersion of this phase and thus the rate of decomposition of the \( \text{H}_2\text{O}_2 \).

On the other hand, the oxidation of \( \text{Mn}^{2+} \) bonded in the zeolite structure may require more severe conditions in terms of pH and pe in comparison with those needed in the bulk solution. It is possible that the manganese when incorporated into a zeolite the +II state of Mn, which is known to be much less active for the decomposition of \( \text{H}_2\text{O}_2 \), is retained to a higher pH. A similar explanation was proposed by Lidén and Öhman [18] in a study on redox stabilization of \( \text{Mn}^{2+} \) and \( \text{Fe}^{2+} \) by co-precipitation with Mg. They found that these cations were stabilized in the +II state when isomorphously substituted for magnesium in carbonate or hydroxide precipitates. It is tempting to interpret the results obtained for zeolite A in these terms, i.e. a preferential exchange into certain sites of the zeolites where the Mn is protected from oxidation, at least at the lowest pH (9.0) studied. An insufficient excess of zeolite may then also result in the partial filling of other exchange sites either active in themselves or unable to prevent the oxidation of \( \text{Mn}^{2+} \) whereas a higher pH may result in the oxidation even of the Mn bound in the prepared sites. This interpretation is however speculative and other explanations for the results obtained may be possible. A further and more thorough analysis of the events directing the catalytic effects in the systems studied will require both additional information about the ion-exchange properties of the zeolites used and an extensive characterization of the nature of the Mn species present in the system at various conditions.

### Conclusions

Zeolites have been proposed as additives in the hydrogen peroxide bleaching of pulp as substitutes for the organic chelating agents currently used for the prevention of the undesired catalytic decomposition of the peroxide by transition metals, mainly manganese. In this preliminary study using a model system containing only \( \text{H}_2\text{O}_2 \), manganese and zeolites it has been shown that the effects of zeolites are rather complicated and that both inhibitive and promoting effects on the catalytic decomposition can be obtained depending upon the conditions used. Provided that these parameters are chosen in an optimal manner, the fundamental requirements for the use of zeolites as inhibitors are, however, fulfilled. The complex nature of the events taking place when adding the zeolite to the model system makes it difficult to draw any general conclusions. Further studies including both the ion-exchange properties of the zeolites used and their effects on the \( \text{H}_2\text{O}_2 \) decomposition are required in order to do so. In spite of the complex nature of the catalytic decomposition in the model system used it should be stressed that this system was chosen in order to make the evaluation as simple as possible. In an industrial pulp bleaching application the situation is further complicated by the presence of the pulp, other additives, dissolved organic substances and various cations present in the bleaching liquor.
Acknowledgements

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References


Use of Zeolites in Hydrogen Peroxide Bleaching of Pulp
Kurt Dyhr and Johan Sterte.
Use of zeolites in hydrogen peroxide bleaching of pulp

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Keywords: Zeolite, Hydrogen peroxide, Decomposition, Bleaching, Transition metal

SUMMARY: The use of zeolites for inhibition of transition metal catalyzed decomposition of hydrogen peroxide was evaluated. A number of zeolite types including zeolites A, P, and Y as well as mordenite 10A were tested as additives in bleaching experiments using a mechanical (TMP) pulp and a chemical (kraft) pulp. For the mechanical pulp, addition of zeolites A and P at a moderate alkali charge resulted in a significant improvement of the bleaching performance as signified by an increase in both brightness and residual peroxide content of the bleaching liquor. The other zeolite types studied did not give any positive effects at the bleaching conditions used. For the chemical pulp, no significant improvements were obtained at any alkali charge using zeolite A as an additive. At high alkali charges addition of zeolite A resulted in a substantially lower brightness than that reached for in a zeolite free reference experiment.

The effects of zeolite addition upon the bleaching of pulp are complex and dependent upon a number of factors. Parameters of great importance are the bleaching pH, consistency and the zeolite type and charge.

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Hydrogen peroxide bleaching is today extensively used for bleaching of mechanical as well as chemical pulp. The utilization of the peroxide in the bleaching process is limited by an undesired decomposition of the peroxide catalyzed by transition metals such as Cu, Fe and Mn. Of these metals manganese has the most deleterious effect mainly due to the fact that Mn is present in a higher concentration in the pulp but also because Fe and Cu are stronger complexed with wood components (Colodette, Dence 1989). Currently, this problem is usually handled by a removal of the transition metals from the pulp using a chelating agent such as EDTA or DTPA to facilitate the removal in a pressing or washing procedure. The effect of the metals remaining after this treatment is minimized by the use of chemical additives such as water soluble silicates or magnesium salts inhibiting the catalytic effects of the metals.

During the last few years a number of patents (von Raven et al. 1989; Leonhardt et al. 1993) and technical papers (von Raven et al. 1989; Sain, Denault 1996; Rivard et al. 1997) have appeared proposing zeolites as an alternative or complement to chelating agents for the control of transition metal catalyzed decomposition of hydrogen peroxide in the bleaching of mechanical pulp. This is not surprising since zeolites are known to be efficient and selective ion-exchangers. Large volumes of zeolites A and P are, for example, used as substituents for phosphates in laundry detergents. A major difference
between zeolites and organic complexing agents is that the former are solid materials which cannot be effectively removed from the pulp in a washing or pressing procedure. A prerequisite, in addition to an excellent ion-exchange selectivity, for zeolites to function in this application is thus that they are able to inhibit the catalytic activity of the transition metal ions, once these ions are bound to the ion-exchange sites of the material.

Essentially all research on the use of zeolites for this purpose reported so far has concerned the use of zeolite A, in most cases in chemically modified forms or in combination with various additives, in bleaching of mechanical pulps. Von Raven et al. (1989) claimed that a system based on zeolite A in combination with sodium carbonate (or sodium hydrogen carbonate) increased the brightness when bleaching a mechanical pulp with hydrogen peroxide with up to 10%, the result depending upon the amount of zeolite and additional additives, such as DTPA and sodium silicate, used. In a technical paper (von Raven et al. 1991) this system (although the zeolite type is not specified) is reported to perform excellent in two different field tests. Leonhardt et al. (1993) claimed a process using zeolites in combination with a chelating agent with a lower affinity to the transition metal ions than the zeolite. A system of this type consisting of modified salts of citric and gluconic acid in combination with zeolite A, was also described by Rivard et al. (1997). Sain and Denault (1996) showed that zeolite based stabilizer systems may be interesting alternatives to chelating agents in the bleaching of recycled newsprint.

The technical nature of the work reported and the fact that most work has been limited to zeolite A, often in rather complex proprietary systems making it very difficult to judge the effect induced by the zeolite itself, motivates a more systematic study focusing on the effects of the zeolites per se in this application.

In a study preceding the present one (Dyhr, Steile 1998) the effects of zeolite addition on the kinetics of manganese catalyzed hydrogen peroxide decomposition was investigated in a simple model system. This study showed that, depending mainly upon the pH, the amount of zeolite added and the zeolite type, zeolite addition can result in a significant inhibition of the catalytic effect but also in a relatively strong promotion of this effect.

The current paper reports on an investigation of the effects of zeolite addition on hydrogen peroxide bleaching of pulp using a number of different zeolite types at various bleaching conditions in terms of alkali-, peroxide-, and zeolite charge.

**Experimental**

**Materials**

Hydrogen peroxide (30 wt%) with a metals content specified to be - Mg <0.000005wt%, Mn <0.000001wt%, Cu <0.000001wt%, Fe <0.000001wt%, and Ca <0.000002wt% - was obtained from Riedel de Haen. The sodium hydroxide used (Ridel de Haen) was specified to contain <0.001 wt% Ca, <0.001wt% Cu, and <0.001 wt% Fe and the sulfuric acid (Riedel de Haen) <0.000005 wt% Mg, <0.000005wt% Mn, <0.00001 wt% Cu, <0.00001 wt% Fe, and <0.0002 wt% Ca. DTPA (p.a.) was obtained from Aldrich Chemie.

The zeolites used in this study were: zeolite A (Wessalith P, Degussa AG), zeolite P (Crossfield), Mordenite 10A (Akzo Nobel AB), and zeolite Y (Akzo Nobel AB)
The mechanical pulp used was a spruce TMP sample taken out after the second disc refiner in the Hallsta Paper Mill, Sweden. Elemental analysis showed a metal content (on dry pulp) of 2170 ppm Ca, 94 ppm Mn, 1 ppm Cu, 9 ppm Fe, and 191 ppm Mg. The chemical pulp used was a kraft pulp sample obtained from AssiDomän Kraftliner, Piteå, Sweden. Elemental analysis of this sample showed a metal content of 1247 ppm Ca, 100 ppm Mn, 1.0 ppm Cu, 5.6 ppm Fe, and 156 ppm Mg.

Bleaching experiments
An amount of distilled water calculated to give a final solids content of 3.0 wt% was charged into a 2 l glass beaker placed on a heating plate, equipped with a mechanical stirrer and a temperature control unit. The water was thereafter heated to 70°C. An amount of zeolite corresponding to 0-5 wt% of dry pulp and 30 g pulp (calculated as oven dry) was then added and the pH was adjusted to 7.2 by addition of either dilute sodium hydroxide or sulfuric acid. The pulp was treated in this solution, maintaining a temperature of 70°C and a pH of 7.2, under continuous stirring for 60 min. Separation of the pulp from the solution was accomplished by pressing with a cotton cloth until an approximate solids content of 30 wt% was reached. The pulp was thereafter placed in a polyethylene bag and reheated to 70°C in a water bath. A sodium hydroxide solution with a concentration calculated to give the desired alkali content (0-2 wt% on dry pulp) and a final solids content of 10 wt% was preheated to 70°C. The pulp and the hydroxide solution was mixed with an amount of hydrogen peroxide corresponding to 1-4 wt% (on dry pulp), using a polyethylene beaker as a mixing vessel. The mixture was stirred vigorously for 30 s, transferred to a polyethylene bag and placed in the water bath at 70°C for 3 h. After completion of the bleaching experiment, the pulp was removed from the plastic bags and rapidly separated from the bleaching solution by suction filtration. The pH and residual content of hydrogen peroxide were then determined. Hydrogen peroxide was determined by iodometric titration and the brightness of the pulp was measured according to a standard procedure (SCAN 11:75).

Results and discussion
Effects of zeolite charge
A series of experiments was performed in order to evaluate the influence of the amount of zeolite used in the bleaching on the peroxide consumption and on the bleaching result and to establish a suitable zeolite charge for the subsequent experiments. The charge of zeolite A was varied within the range 0-4 wt% (on dry pulp) using an alkali charge of 1.2 wt% and a peroxide charge of 2.0 wt%.

The results of this series are shown in Fig. 1. As seen, the brightness increased with increasing zeolite charge up to a level of approximately 2 wt% and was then essentially constant with a further increase up to 4 wt%. The residual peroxide content in the bleaching liquor (Fig. 2) after completion of the bleaching showed a continuous increase with increasing amount of zeolite added within the range studied, with a slight tendency for the curve to level out at higher zeolite charges. Taking these results into account, a zeolite charge corresponding to 4 wt% (on dry pulp) was selected for the subsequent experiments of the study.
Table 1. Characterization of zeolite samples used

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Structural formula(^a)</th>
<th>CEC(^b) (meq/g)</th>
<th>brightness (%)</th>
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<tr>
<td>A</td>
<td>2SiO(_2) Al(_2)O(_3) Na(_2)O</td>
<td>7.0</td>
<td>96.6</td>
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<tr>
<td>P</td>
<td>2SiO(_2) Al(_2)O(_3) Na(_2)O</td>
<td>7.0</td>
<td>98.6</td>
</tr>
<tr>
<td>Y</td>
<td>5.3SiO(_2) Al(_2)O(_3) Na(_2)O</td>
<td>4.1</td>
<td>98.6</td>
</tr>
<tr>
<td>M 10A</td>
<td>13SiO(_2) Al(_2)O(_3) Na(_2)O</td>
<td>2.1</td>
<td>94.4</td>
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</table>

\(^a\)Calculated from elemental analyses provided by the manufacturers
\(^b\)Calculated for dehydrated zeolites from structural formulae.

Fig. 1. Influence of the addition of zeolite A on the brightness when bleaching a TMP pulp at 70°C for 3 h with a solution initially containing 2 wt% hydrogen peroxide and 1.2 wt% sodium hydroxide.
Fig. 2. Influence of the addition of zeolite A on the residual peroxide level when bleaching a TMP pulp at 70°C for 3 h with a solution initially containing 2 wt% hydrogen peroxide and 1.2 wt% sodium hydroxide.

Effects of alkali content

Fig. 3. Influence of the addition of zeolite A (4 wt%, on dry pulp basis) on the brightness when bleaching a TMP pulp at 70°C for 3h with a solution initially containing 2 wt% hydrogen peroxide and 0.0-2.0 wt% alkali.
A series of experiments was performed in order to study the effects of the alkali content of the bleaching mixture on the brightness of the bleached pulp and the residual peroxide content. In this series a charge of zeolite A corresponding to 4 wt% (on dry pulp) and a peroxide charge of 2.0 wt% was used. For comparison, a reference series using the same experimental conditions but without addition of zeolite was carried out. Fig. 3 shows the brightness as a function of alkali charge obtained in the two series. The optimal alkali charge in the presence of 4 wt% zeolite A was approximately 1 wt% yielding an ISO-brightness of 68%. The corresponding optimum in the absence of zeolite was found at a somewhat lower charge, about 0.6 wt%, and at a brightness level of about 65.5%.

Fig. 4 shows the residual hydrogen peroxide content in the bleaching liquor after bleaching at various alkali charges with and without the use of zeolite A as an additive. As expected, the residual peroxide content decreased with increasing alkali charge in both experimental series. This decrease was, however, significantly less pronounced for the series performed with added zeolite.

![Graph showing residual peroxide content vs alkali charge]

**Effects of the initial hydrogen peroxide content**
A series of experiments was performed in order to investigate the effects of hydrogen peroxide charge on the peroxide consumption and the bleaching result when bleaching mechanical pulp in the presence of 4 wt% zeolite A. For comparison, a corresponding series was performed without the addition of zeolite.
Fig. 5. Influence of the addition of zeolite A (4 wt%, on dry pulp basis) on the brightness when bleaching a TMP pulp at 70°C for 3h with a solution initially containing 1-4 wt% hydrogen peroxide and 1.0 wt% sodium hydroxide.

Fig. 5 shows the influence of the peroxide charge on the brightness of the pulp. In the presence of 4 wt% zeolite A, 2 wt% peroxide was sufficient to attain a maximal brightness of 68%. A further increase in the peroxide charge did not affect the brightness significantly. In the absence of zeolite, a continuous increase of the brightness with increasing peroxide charge was observed with a maximal value obtained at a charge of 4%. The maximal brightness was slightly lower than that reached with addition of zeolite A. Fig. 6 shows the residual peroxide contents in the bleaching solutions after completion of the experiments. In the experiments performed with added zeolite A the residual content increased sharply with the amount added indicating that only a limited amount of the additional peroxide charged above the level of 2.0 wt% was actually consumed in the bleaching process. Without zeolite addition, on the other hand, the increase in residual peroxide content with increasing charge was less pronounced. Judging from the results of these experiments, the peroxide charge required in the absence of zeolite to give the same bleaching result is roughly twice that needed when 4 wt% zeolite A is added.
Fig. 6. Influence of the addition of zeolite A (4 wt%, on dry pulp basis) on the residual peroxide level when bleaching a TMP pulp at 70°C for 3h with a solution initially containing 1-4 wt% hydrogen peroxide and 1.0 wt% sodium hydroxide.

Effects of the consistency in the bleaching stage
Using a zeolite charge of 4 wt% zeolite A, the effects of the consistency on the bleaching of the mechanical pulp was investigated in the range 3-10 wt%. For comparison, a corresponding series of experiments was performed but without addition of zeolite. The results of the experiments are summarized in Table 2. For the zeolite containing samples the brightness increased significantly with an increased consistency. A gain in brightness of more than 4 % was obtained when moving from 3 wt% to 10 wt% consistency. This gain was accompanied with a slight decrease in the residual peroxide content of the bleaching liquor. For the non-zeolite containing samples, both the brightness and the residual peroxide content was essentially constant within the range of consistencies covered in these experiments. Attempts were made to investigate these effects at higher consistencies. These experiments indicated a further increase in the brightness with increasing consistency for zeolite containing samples. The reproducibility of the results was, however, too poor to render them conclusive. This rather poor reproducibility at high consistencies was most likely due to an insufficient mixing attainable in the experimental setup used.
Table 2. Effects of consistency on the residual peroxide content and brightness of TMP pulp bleached in the presence and absence of 4 wt% zeolite A

<table>
<thead>
<tr>
<th>consistency (%)</th>
<th>residual peroxide cont. (wt%)</th>
<th>Brightness (%)</th>
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<tr>
<td></td>
<td>zeolite A</td>
<td>reference*</td>
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<tr>
<td>3</td>
<td>0.80</td>
<td>0.05</td>
</tr>
<tr>
<td>5</td>
<td>0.66</td>
<td>0.04</td>
</tr>
<tr>
<td>10</td>
<td>0.64</td>
<td>0.06</td>
</tr>
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</table>

*Reference samples bleached using identical conditions but in the absence of zeolite

Effects of other zeolite types and conventional chelating agents

In order to investigate whether the effects observed using zeolite A are unique for this zeolite type, a number of common zeolites were tested using a zeolite charge of 4 wt%, a peroxide charge of 2 wt% and three different levels of alkali charge. The results of these tests, see Table 3, showed that zeolite P resulted in an inhibition of the catalytic peroxide decomposition whereas the other zeolites tested apparently had little or no effect on the bleaching performance. In the case of zeolite Y at the lowest alkali charge used, the results in terms of brightness and residual peroxide were even deteriorated in comparison with those obtained for the reference sample. For comparison, experiments were also made using 0.2 wt% of EDTA and DTPA instead of zeolites. As seen in Table 3, the addition of these conventional chelating agents resulted in an improvement of the bleaching result that somewhat surpassed the best results obtained with zeolite addition (zeolite A). The difference is particularly notable at the highest alkali charge investigated whereas the results achieved with zeolite A at lower alkali charges were closer to those reached with the conventional chelating agents.
Table 3. Influence of the addition of 4 wt% (on dry pulp basis) of various zeolites on the brightness and residual peroxide content when bleaching a TMP pulp at 70°C with a solution initially containing 2 wt% hydrogen peroxide and 0.4-1.6 wt% alkali.

<table>
<thead>
<tr>
<th>Allkali content (wt%)</th>
<th>Brightness (%)</th>
<th>Residual peroxide (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0.6</td>
<td>1.6</td>
</tr>
<tr>
<td>0.4</td>
<td>1.0</td>
<td>1.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Brightness (%)</th>
<th>Residual peroxide (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference\textsuperscript{a}</td>
<td>65.1</td>
<td>61.6</td>
</tr>
<tr>
<td>zeolite A</td>
<td>65.4</td>
<td>68.3</td>
</tr>
<tr>
<td>zeolite P</td>
<td>64.7</td>
<td>67.0</td>
</tr>
<tr>
<td>mordenite 10A</td>
<td>65.8</td>
<td>63.5</td>
</tr>
<tr>
<td>zeolite Y</td>
<td>63.0</td>
<td>61.6</td>
</tr>
<tr>
<td>EDTA\textsuperscript{b}</td>
<td>66.1</td>
<td>68.8</td>
</tr>
<tr>
<td>DTPA\textsuperscript{b}</td>
<td>66.1</td>
<td>69.3</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reference sample bleached using identical conditions but in the absence of zeolite.
\textsuperscript{b}EDTA and DTPA were charged in amounts corresponding to 0.20 wt% of dry pulp.

Effects of zeolite addition on the peroxide bleaching of chemical pulp
A number of experiments were performed in order to assess the possibility of using zeolites as substitutes for organic chelating agents in the bleaching of kraft pulp. Some representative results obtained using a 4.0 wt% charge of zeolite A and varying the alkali charge, are shown in Table 4. At the lowest alkali charge investigated, a modest positive effect of zeolite addition was observed as signified by a higher residual peroxide content in the bleaching liquor. The brightness obtained at these conditions was, however, slightly lower than that reached in the absence of zeolite. When increasing the alkali charge the difference between the bleaching results in the presence and in the absence of zeolite was even more pronounced and at a charge of 1.6% the difference in ISO-brightness was almost 10%. These results as well as other results obtained for bleaching of chemical pulps in our laboratory (not presented here) in the presence of zeolites indicated that the zeolites in most instances not have a positive effect on the
bleaching performance of the peroxide. An explanation could be the fact that, at high pH levels, the zeolite appears to promote rather than inhibit the catalytic action of the manganese the presence of which is believed to be the primary cause of peroxide decomposition (Dyhr, Sterte 1998).

Table 4. Influence of the addition of 4 wt% (on dry pulp basis) of zeolite A on the brightness, residual peroxide content and final pH when bleaching a kraft pulp at 70°C with a solution initially containing 4 wt% hydrogen peroxide and 0.4-1.6 wt% alkali.

<table>
<thead>
<tr>
<th>Alkali content (wt%)</th>
<th>0.4</th>
<th>1.0</th>
<th>1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brightness (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zeolite A</td>
<td>67.5</td>
<td>63.8</td>
<td>64.0</td>
</tr>
<tr>
<td>reference*</td>
<td>68.5</td>
<td>71.9</td>
<td>73.8</td>
</tr>
<tr>
<td>Residual peroxide (wt%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zeolite A</td>
<td>0.67</td>
<td>0.11</td>
<td>0.00</td>
</tr>
<tr>
<td>reference*</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Final pH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zeolite A</td>
<td>10.3</td>
<td>11.1</td>
<td>11.9</td>
</tr>
<tr>
<td>reference*</td>
<td>9.8</td>
<td>11.1</td>
<td>11.8</td>
</tr>
</tbody>
</table>

*Reference sample bleached using identical conditions but in the absence of zeolite.
Discussion
As mentioned in the introduction, the present investigation was preceded by a study of the effects of zeolites on the manganese catalyzed decomposition of hydrogen peroxide in a simple model system and in the absence of pulp (Dyhr and Steile, 1998). Despite the simplicity of that system the effects of zeolite addition were found to be rather complex. In short, certain zeolites such as mordenite 10A show a significant inhibitive effect on the decomposition rate at relatively high pH and a promotive effect at lower pH values (pH 9-10). Other zeolite types such as zeolite Y show no inhibiting effects at any pH in the range investigated. A third group of zeolites including zeolites A and P show a promotive effect on the catalytic decomposition at high pH values but act as inhibitors at lower ones. When added in relatively large amounts, the inhibitive effect of zeolite A at a pH of 9.0 is quite remarkable. The results of this basic study are interpreted in terms of the ion-exchange capacity and selectivity of the zeolites investigated.

Systems containing pulp are inherently much more complex than the model system used in the preliminary experiments. In addition to manganese ions, the pulp contains a matrix of other cations as well as a variety of soluble organic compounds in the aqueous phase. Some of these cations, eg. Ca, Mg and Na are present in concentrations exceeding that for Mn and will compete with the Mn ions for the ion-exchange sites of the zeolite. For the prevalent cation in the matrix, Ca²⁺, this competition should be rather successful, as most zeolites (particularly zeolite A) are known to be rather selective for calcium ions. Moreover, trace amounts of other transition metal ions, mainly Fe and Cu, are present in the matrix. The influence of zeolites on the catalytic effect of these metals is not known and may in fact be anything from strongly inhibitive to strongly promotive.

The presence of soluble organic compounds in the matrix may also influence the effects of the zeolite as zeolites are known to be good sorbents and most likely will adsorb these substances to some extent limiting the utilization of the zeolite as a cation-exchanger. A competition which further complicates the situation will also exist between the exchange sites on the pulp surface and those within the zeolite structure.

The amount of zeolite required to give a substantial effect in the bleaching of mechanical pulp was about 4 wt% (on dry pulp). Using the content of Mn as a basis, this was approximately twenty times as much as the amount needed to obtain a maximal effect in the model system. Although all the factors discussed above will affect the impact of zeolite addition in peroxide bleaching the most important one, explaining this difference is probably the relatively high content of Ca ions in the pulp.

In the model experiments (Dyhr, Steile 1998), a strong pH dependence of the effects of zeolite addition on the kinetics of Mn-catalyzed peroxide decomposition was observed. For zeolite A, a strong inhibitive effect was obtained at a pH of 9.0 whereas the effect at higher pH values was promotive. In the bleaching experiments using mechanical pulp, the initial pH is in the range 11.5-10.5 depending upon the alkali charge. The pH then drops during the experiment to a final value in the range 7.5-8.8. Despite the compositional differences between the experimental systems of the present study and the model systems, the general trends are similar. Positive effects of zeolite addition were only obtained in systems with relatively low alkali charges. In fact, the initial pH in the most successful experiment was 10.5. This pH dropped rather quickly to a level near 9.0 (ca. 30 min) and then gradually to a final pH of about 8 (3h).
The somewhat disappointing results obtained for the kraft pulp can also be interpreted in terms of pH. Although no significant enhancement was obtained in any of these experiments the most positive results were obtained at the lowest alkali charge investigated (0.4 wt%). A difference between the experiments involving kraft pulp and those using mechanical pulp was that the pH level in the former was generally considerably higher. Although this study clearly showed that zeolites can be used to improve the bleaching performance of hydrogen peroxide, the improvement was limited in comparison with that obtained using chelating agents and, furthermore, relatively large amounts of zeolite were required. The results did, however, also suggest a number of improvements that may render zeolites more competitive. The presence of calcium competing with the transition metal ions for the ion-exchange sites of the zeolite and thus affecting the utilization of the zeolite in a negative manner may be possible to handle by an additive forming an insoluble compound with calcium ions or by the use of a complementary (bio-degradable) chelating agent. A comparison between the results obtained in the model system with those of the actual bleaching experiments suggest that most of the peroxide consumption in the latter may have taken place at the high initial pH level at which zeolite A does not show any inhibitive effect on the peroxide decomposition. The use of a buffer agent in addition to the zeolite in order to avoid the high initial pH may affect the utilization of the zeolite in a positive way.

As mentioned in the introduction, a number of patents and technical papers (von Raven et al. 1989, 1991; Leonhardt et al. 1993; Sain, Denault 1996; Rivard et al. 1997) describing the utilization of zeolites in combination with other additives to facilitate the utilization of hydrogen peroxide in the bleaching of mechanical pulp have been published. Most of these additional additives appear to have either a buffering or a chelating function.

**Conclusion**

The use of zeolites in the hydrogen peroxide bleaching of pulp was evaluated. For a mechanical pulp, addition of zeolite A, and to some extent zeolite P, resulted in a significant improvement of the bleaching as signified by a higher ISO-brightness and a decrease in the peroxide consumption. In order for this improvement to be realized, a relatively low charge of alkali was required. Other zeolite types studied did not affect the bleaching process in a positive direction. For a chemical pulp, no significant improvement was obtained at any of the conditions investigated. The pH during the bleaching process appeared to be of major importance for the effects of zeolite addition. From the results obtained in this study, zeolites alone do not seem to be viable substitutes for the chelating agents currently used to minimize the transition metal catalyzed decomposition of hydrogen peroxide in bleaching processes. Systems containing additional additives in combination with zeolites may be more competitive in this respect.
Acknowledgments

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Literature

Use of Zeolites to Inhibit the Transition Metal Catalysed Decomposition of $\text{H}_2\text{O}_2$ in the Bleaching of Pulp

Kurt Dyhr and Johan Sterte.

Submitted to 12th International Zeolite Conference, Baltimore, Maryland, USA, July 5-10, 1998.
USE OF ZEOLITES TO INHIBIT THE TRANSITION METAL CATALYZED DECOMPOSITION OF H₂O₂ IN THE BLEACHING OF PULP

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The effects of zeolites A, P, Y, and mordenite on the transition metal catalyzed decomposition of hydrogen peroxide was studied, both in the absence of pulp in a model system and in laboratory bleaching of a mechanical pulp. In the model system, both inhibitive and promotive effects were obtained depending primarily upon the pH and the type and amount of zeolite. At a pH of 9.0, addition of zeolite A resulted in a tremendous decrease in the decomposition rate if added in large excess. In the bleaching experiments, addition of zeolites A and P resulted in a marked improvement of the brightness and a decrease in the peroxide conversion whereas the other zeolites studied showed little or no effects. A comparison between the two experimental series is made and the role of the zeolite in peroxide bleaching is discussed.

INTRODUCTION

A novel area in which the use of zeolites has been proposed is in the hydrogen peroxide bleaching of pulps. Both patents and technical reports [1,2] describing zeolite-based additives for this purpose have appeared in the last few years.

Most manufacturers of pulp in Europe are abandoning chlorine containing bleaching agents due to environmental considerations and turning to bleaching sequences involving one or more steps in which hydrogen peroxide is the active chemical. A problem with the use of hydrogen peroxide is that some transition metals (mainly Mn) present in the pulp catalyze the undesired decomposition of the peroxide, thus severely limiting the utilization of the bleaching potential. To limit the decomposition, these metals are usually removed using a chelating agent such as EDTA or DTPA. The fact that these chelating agents are both expensive and questionable from an environmental viewpoint is a strong motive to search for alternative solutions, thus the interest in zeolites. In order for a zeolite to become an alternative, a large cation-exchange capacity and a good selectivity for the transition metals of interest is a necessary prerequisite. Since the zeolite is a solid material it cannot be effectively removed from the pulp by washing. A further requirement is therefore that the transition metal containing zeolite is not catalytically active for the decomposition of the peroxide.
The present paper reports on a study of the effects of a number of zeolites on the transition metal catalyzed decomposition of hydrogen peroxide, both in a simple model system and in laboratory bleaching of a mechanical pulp.

EXPERIMENTAL

The zeolites used in this study were: zeolites A (Degussa), P (Crossfield), Y (Akzo Nobel) and Mordenite 10A (Akzo Nobel). The mechanical pulp used was a spruce TMP sample from the Hallsta Paper mill, Sweden. Elemental analysis (on dry pulp): 2170 ppm Ca, 94 ppm Mn, 1 ppm Cu, 9 ppm Fe, and 191 ppm Mg.

A simple model system was used to study the effects of various zeolites on the Mn-catalyzed decomposition of H₂O₂. A glass beaker was charged with an aqueous solution containing an amount of Mn calculated to give a final concentration of 0.25-4.0 ppm and heated to 70°C. An amount of zeolite in excess of 2-5 times of the Mn on a CEC-basis was added. After 30 min contact time, the pH was raised to 9.0-10.8 and H₂O₂ corresponding to a final concentration of 0.010M was added.

Bleaching of the mechanical pulp was performed as follows. An amount of distilled water calculated to give a final pulp content of 3.0 wt% was heated to 70°C after which zeolite (0-5 wt%, on dry pulp) and 30 g (dry) pulp was added. The pH was adjusted to 7.2 and maintained at a temperature of 70°C for 60 min. The pulp was then separated form the solution by pressing to obtain a solids content of about 30 wt%. An NaOH solution, preheated to 70°C, calculated to give a final NaOH content of 0-2 wt% (on dry pulp) and a pulp content of 10 wt% was added. The resulting slurry was mixed with an amount of hydrogen peroxide corresponding to 1-4 wt% (on dry pulp) and transferred to polyethylene bags which were placed on a water bath at 70°C for 3 h. After completion, the pulp was removed from the polyethylene bags, separated from the bleaching solution and cooled.

Peroxide contents were determined by iodometric titration and the brightness of the bleached pulp was measured according to a standard procedure (SCAN 11:75).

RESULTS AND DISCUSSION

A large number of experiments was performed with the model system in order to evaluate the effects of various zeolites on the manganese catalyzed decomposition of H₂O₂. Among the variables studied, the pH, the zeolite type and the amount of zeolite charged in relation to the manganese content were found to be the most important. Three of the four zeolites showed inhibitive effects on the decomposition at certain conditions of pH and zeolite charge. At the highest pH studied (10.8), Mordenite 10A was found to inhibit the catalytic effect significantly whereas the other zeolites showed little or no effect. The decomposition was found to be a first order reaction with a rate constant of 0.136 min⁻¹ in the absence of zeolite and 0.049 min⁻¹ in the presence of Mordenite. At the lower pH levels investigated (9.9 and 9.0), Mordenite, at a 2:1 ratio (on a CEC basis) to Mn²⁺, promoted the catalytic effect.
significantly. At the intermediate pH (9.9) zeolite A, at a 2:1 ratio, resulted in a substantial promotion of the decomposition. The most interesting results were obtained using zeolite A at a pH of 9.0. Figure 1 shows the rate of decomposition of H₂O₂ at this pH in the presence of 1.0 ppm Mn and various amounts of zeolite A. A ratio of 2:1 resulted in a promotive effect whereas the rate decreased dramatically with an increased charge.

A series of bleaching experiments was performed in order to evaluate the effects of zeolite addition on the brightness and the peroxide conversion in the bleaching of pulp using the alkali charge, the H₂O₂ charge and the type and amount of zeolite as process variables. Upon addition of zeolite A in a system charged with 1.2 wt% NaOH and 2.0 wt% H₂O₂ (both on dry pulp) the brightness increased with increasing zeolite charge up to 2 wt% (on dry pulp) and then remained constant. The peroxide conversion decreased with increasing zeolite charge up to 4 wt%. The optimal alkali charge was higher using zeolite A (1.0 wt%) than in the absence of zeolite (0.6 wt%). Using the optimal conditions for zeolite A and a peroxide charge of 2.0 wt%, a number of zeolites were evaluated. Results are summarized in table 1. Zeolites A and P result in a significant improvement of the brightness and a deceased conversion of H₂O₂. Zeolite Y and Mordenite do not improve the results.

For the bleaching of pulp with H₂O₂, the initial pH is about 10.5. Within the first 10 minutes, the pH drops from the initial value to approximately 9.5. A pH of 9 is reached after about 30 min and the final pH after 3 h of bleaching is around 8. For the model system experiments it was noted that Mordenite resulted in an inhibition

![Figure 1. Effects of zeolite A at different ratios (on a CEC-basis) on the conversion of H₂O₂ at pH 9.0 in the presence of 1.0 ppm Mn.](image-url)
Table 1.
Effects of zeolite addition on the brightness and hydrogen peroxide conversion in the bleaching of a mechanical pulp.

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Brightness (%-ISO)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>no addition</td>
<td>61.6</td>
<td>97</td>
</tr>
<tr>
<td>zeolite A</td>
<td>68.3</td>
<td>68</td>
</tr>
<tr>
<td>zeolite P</td>
<td>67.0</td>
<td>75</td>
</tr>
<tr>
<td>zeolite Y</td>
<td>61.6</td>
<td>100</td>
</tr>
<tr>
<td>mordenite 10A</td>
<td>63.5</td>
<td>99</td>
</tr>
</tbody>
</table>

at pH 10.8 but not at the lower pH values studied, whereas zeolite A resulted in an inhibition at pH 9.0 but promoted the Mn at higher pH values. The fact that addition of zeolite A in the bleaching experiments results in an improvement of the brightness as well as of the peroxide conversion implies that the inhibitive effect at low pH brought about by the addition of zeolite exceeds the promoting effect at a higher pH. This is reasonable since the pH during the main part of the bleaching is close to 9.

In the model experiments, the solution contains only the peroxide and the manganese salt. In the bleaching of pulp, on the other hand, a matrix of different cations as well as organic compounds is present in the aqueous phase. Several of these other cations, eg. Ca$^{2+}$, Mg$^{2+}$, Na$^+$, are present in high concentrations and will compete for the exchange sites of the zeolites. The matrix also contains trace amounts of other transition metals, mainly Cu and Fe, which also are known to catalyze the peroxide decomposition. This, and the fact that the pulp itself is an ion-exchanger, makes the situation complicated. Comparing the model system with the bleaching of pulp, about twenty times more zeolite is required in the latter case to achieve a maximal effect. The large difference is probably due to the factors discussed above.

CONCLUSION

This study shows that zeolites can be used to improve the bleaching performance of hydrogen peroxide. The improvement is limited in comparison with that obtained using chelating agents and relatively large amounts of zeolite are required. The results do, however, suggest a number of improvements that, if pursued, may render zeolites more competitive.

REFERENCES
The effects of zeolites on the manganese catalysed decomposition of hydrogen peroxide was evaluated both in the absence of pulp in a simple model system and in laboratory bleaching of a mechanical and a chemical pulp where the ISO-brightness and residual peroxide level were determined. The model system showed that the system is very complex and that zeolites can have either inhibitive or promoting effects on the decomposition of hydrogen peroxide depending on the pH, type of zeolite and the stochiometric ratio between manganese and the zeolite. Zeolite A, the most commonly investigated zeolite showed clear inhibitive effect of the decomposition of hydrogen peroxide at pH 9.0.

The bleaching experiments showed that zeolites A and P result in a marked improvement of the bleaching result of a TMP (termo mechanical pulp) pulp. No significant enhancement of the bleaching results was obtained with the chemical pulp.